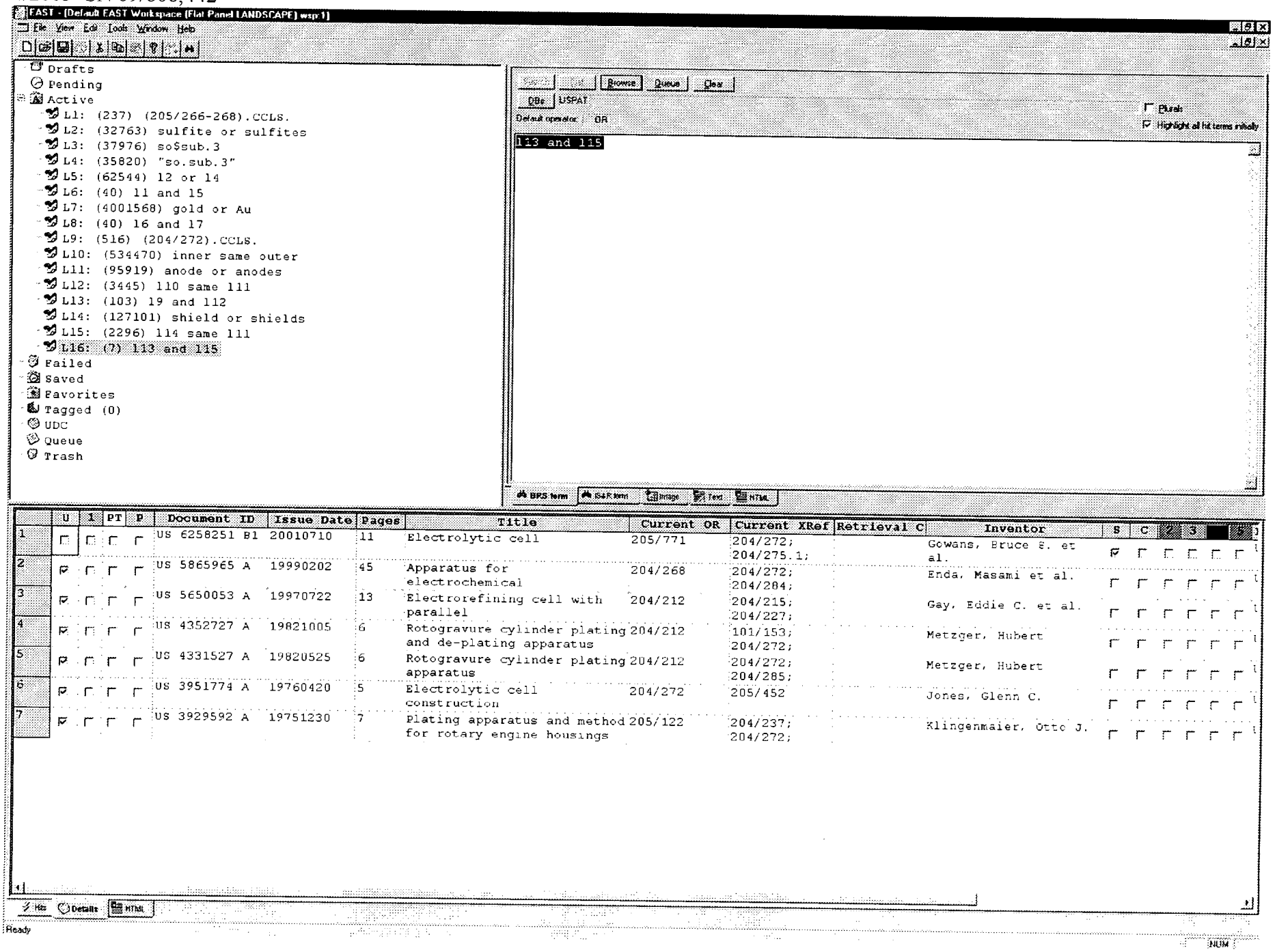


	U	1	PT	P	Document ID	Issue Date	Pages	Title	Current OR	Current XRef	Retrieval C	Inventor	S	C	2	3
1	☐	☐	☐	☐	US 6258251 B1	20010710	11	Electrolytic cell	205/771	204/272; 204/275.1;		Gowans, Bruce S. et al.	☑	☐	☐	☐
2	☑	☐	☐	☐	US 5865965 A	19990202	45	Apparatus for electrochemical	204/268	204/272; 204/284;		Enda, Masami et al.	☐	☐	☐	☐
3	☑	☐	☐	☐	US 5650053 A	19970722	13	Electrorefining cell with parallel	204/212	204/215; 204/227;		Gay, Eddie C. et al.	☐	☐	☐	☐
4	☑	☐	☐	☐	US 4352727 A	19821005	6	Rotogravure cylinder plating and de-plating apparatus	204/212	101/153; 204/272;		Metzger, Hubert	☐	☐	☐	☐
5	☑	☐	☐	☐	US 4331527 A	19820525	6	Rotogravure cylinder plating apparatus	204/212	204/272; 204/285;		Metzger, Hubert	☐	☐	☐	☐
6	☑	☐	☐	☐	US 3951774 A	19760420	5	Electrolytic cell construction	204/272	205/452		Jones, Glenn C.	☐	☐	☐	☐
7	☑	☐	☐	☐	US 3929592 A	19751230	7	Plating apparatus and method for rotary engine housings	205/122	204/237; 204/272;		Klingenmaier, Otto J.	☐	☐	☐	☐

EAST Browser - L18: (96) 13 and 16 | US 4872959 | Tag: 5 | Doc: 44/96 (SORTED) | "Full" 2/16 (Total images 16)

File Edit View Tools Window Help

	Document ID	Pages	1	2	3	4	U	S	C	P	Kind Codes	Sou
39	US 5154807 A	11										USPAT
40	US 5102522 A	11										USPAT
41	US 5002649 A	15										USPAT
42	US 4929327 A	5										USPAT
43	US 4891115 A	18										USPAT
44	US 4872959 A	16										USPAT
45	US 4853099 A	15										USPAT

US-PAT-NO: 4872959

DOCUMENT-IDENTIFIER: US 4872959 A
See image for Certificate of Correction

TITLE: Electrolytic treatment of liquids

---------- KWIC ----------

Abstract Text - ABTX (1):

An improved electrolytic system for treating aqueous solution which passes the solution along an inner helical insulator wrapped around a centrally located anode solid rod and an enclosing inner cathode tube, then along a cathode tube wrapped or spaced with another helical insulator and an enclosing outer anode tube. The solid rod can be replaced with an innermost tube in order for the solution to initially pass through a cathode portion of the system. Also, the innermost cathode tube can have a plurality of apertures as passageways for the solution. A DC voltage is applied, in one direction or in sequential fields of different directions across the plurality of metal rods and tubes, thereby effectively removing both suspended materials and dissolved solids from the aqueous solution to be treated. The power supply required from the DC voltage can be decreased by treating specified tubes or rods. Various materials may be removed from waste water, either with the improved apparatus and method of the new apparatus of this invention or with the Liggett device, including removal of organics, or rendering plant fats, colloids, salts or the recovery of certain metals including gold.

Brief Summary Text - BSTX (26):

In an embodiment of said electrolytic treatment apparatus, said centrally located member is solid. In a further refinement, said centrally located member is tubular. The tubular centrally located member has a plurality of apertures passing therethrough in a further aspect of the invention. In another aspect, said centrally located member and said outer tube are made of materials which act as anodes, and wherein said inner tube is made of material which act as a cathode. In a preferred embodiment, said centrally located member and said outer tube are made of materials which act as cathodes, and wherein said inner tube is made of material which act as an anode .

Brief Summary Text - BSTX (27):

In a further preferred embodiment of the electrolytic treatment apparatus constituting the first aspect of the invention, said centrally located member is made of a material which acts as cathode, and wherein said inner and outer tubes are made of materials which act as anodes .

Brief Summary Text - BSTX (28):

In a further preferred embodiment of the electrolytic treatment apparatus constituting the first aspect of the invention said centrally located member is made of a material which acts as anode, and wherein said inner and outer tubes are made of materials which act as cathodes.

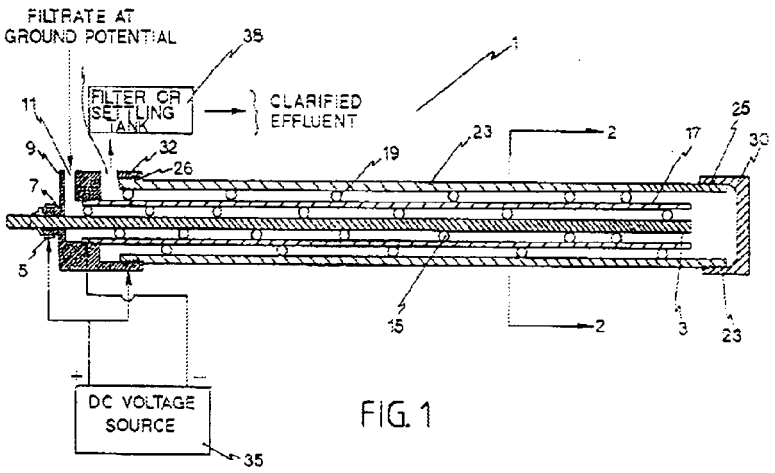


FIG. 1

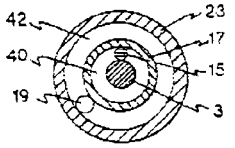


FIG. 2

FAST Browser - L18: (96) 13 not 16 | US 5882502 | Tag: S | Doc: 13/96 (SORTED) | "Full" 5/22 (Total images 22)

File Edit View Tools Window Help

	Document ID	Pages	1	2	3	4	U	S	C	P	Kind Codes	Sou
8	US 6126797 A	40										USPAT
9	US 6117285 A	32										USPAT
10	US 6103076 A	19										USPAT
11	US 6007686 A	23										USPAT
12	US 5972180 A	8										USPAT
13	US 5882502 A	22										USPAT
14	US 5873986 A	9										USPAT

US-PAT-NO: 5882502

DOCUMENT-IDENTIFIER: US 5882502 A

TITLE: Electrochemical system and method

---------- KWIC ---------

Detailed Description Text - DETI (14):

The cell comprises an annular body in which the outer surface 40 provides the cathode or anode wall and the inner well 41 provides the respective solution electrode. It is possible to add another inner ring (not shown) to act as another cathode or anode, further increasing the capacity of the cell. Tangential inlets 42 and outlets 43 may be provided to give turbulent flow and good mixing in the cells. A non-conductive lid 44 is used in the cell and electrical connections are provided to the anode /cathode and the solution electrode.

Claims Text - CLTX (12):

7. An electrochemical metal recovery apparatus as in claim 1 wherein either the anode cell or the cathode cell or both the anode cell and cathode cell comprises an annular body having inner and outer cylindrical walls defining the annular body therebetween, the outer cylindrical wall being the anode or cathode respectively and the inner cylindrical wall being the respective solution electrode, and wherein a tangential electrolyte inlet is provided at one axial end of the annular body and a tangential electrolyte outlet at the other axial end of the annular body.

Current US Cross Reference Classification - CCXR (8):

204/272

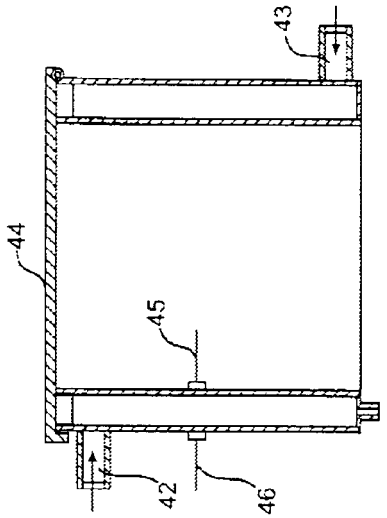


FIG. 4B

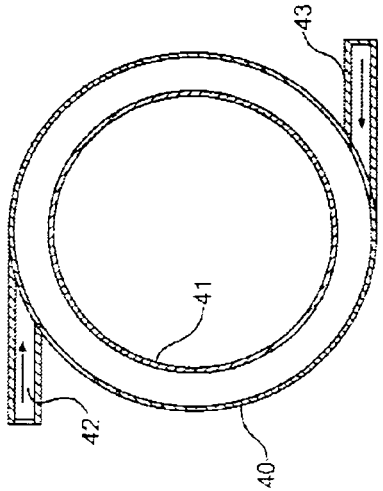


FIG. 4A

EAST Browser - [16: (7) 13 and 15] [US 5865965 A] [Tag: S] [Doc: 2/7 (SORTED)] [Format: KWIC]

File Edit View Tools Window Help

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3	US 5650053 A	13											USPAT
4	US 4352727 A	6											USPAT
5	US 4331527 A	6											USPAT
6	US 3951774 A	5											USPAT
7	US 3929592 A	7											USPAT

US-PAT-NO: 5865965

DOCUMENT-IDENTIFIER: US 5865965 A

TITLE: Apparatus for electrochemical decontamination of radioactive metallic waste

---------- KWIC ---------

Abstract Text - ABTX (1):

An insulating shield plate (1) divides a room of an electrolysis bath (2) into an anode chamber (13) and a cathode chamber (14). An anode (5) is disposed in the anode chamber (13), and a cathode (6), metallic waste (7) and heater (4) are disposed in the cathode chamber (14). An electrolyte (3) stored in the electrolysis bath (2) flows in a circulation path from a circulating pump (10) through a circulating line (12) and filter (11) to return the electrolysis bath (2). An exhaust gas processing device 9 is connected to the electrolysis bath (2). When a voltage is supplied to the anode (5) and cathode (6), a surface of the metallic waste (7) is charged in a positive polarity to dissolve a base metal of the metallic waste (7). Further, a cylindrical anode (33) is arranged in an electrolyte (32) in an electrolysis bath (31), and a cylindrical metal (34) as a metallic waste is arranged in the cylindrical anode (33). After a bar-shaped cathode (35) is arranged in the cylindrical metal (34), a DC voltage is supplied to the cylindrical anode (33) and the bar-shaped cathode (35). At this time, the system may be constructed in that oxygen occurs by charging in a positive polarity in an inner surface of the cylindrical metal (34) and the base metal of the cylindrical shape is dissolved.

Brief Summary Text - BSTX (19):

an insulating shield plate for dividing a room of the electrolysis bath into an anode chamber and a cathode chamber, and the insulating shield plate which is set in a U-shape along three inner wall surfaces of the electrolysis bath.

Brief Summary Text - BSTX (33):

any one of electrodes of two kinds of the anode and the cathode for electrolysis has a cylindrical shape along the outer shape of the metallic waste having a curved portion, and the other of the electrodes is formed in a bar-shaped in correspondence with an inner shape of the metallic waste.

Brief Summary Text - BSTX (43):

a cylindrical anode which is arranged on an inner wall of the cylindrical insulating shield body;

Brief Summary Text - BSTX (53):

an anode which is arranged at the bottom of the insulating shield vessel;

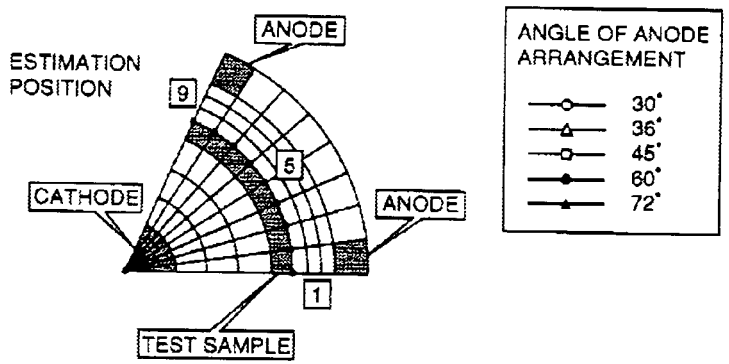


FIG.31A

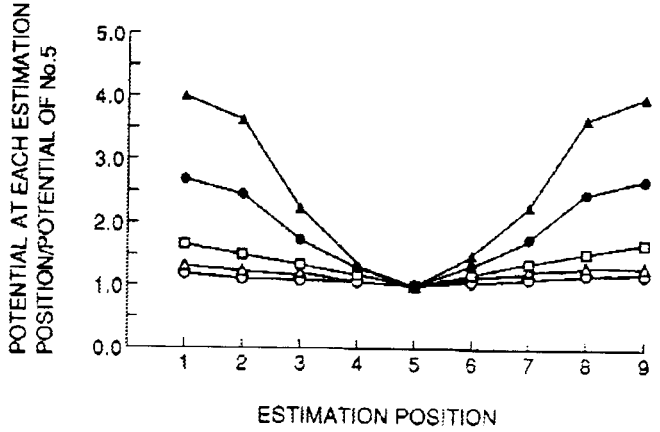


FIG.31B

EAST Browser - L16: (7) 13 and 15 | US 5865965 | Tag: S | Doc: 2/7 (SORTED) | "Full" 27/45 (Total images 45)

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	Document ID	Pages	1	2	3	4	5	U	S	C	P	Kind Codes	Sou
1	US 6258251 B1	11							☑				USPAT
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3	US 5650053 A	13						☑					USPAT
4	US 4352727 A	6						☑					USPAT
5	US 4331527 A	6						☑					USPAT
6	US 3951774 A	5						☑					USPAT
7	US 3929592 A	7						☑					USPAT

US-PAT-NO: 5865965

DOCUMENT-IDENTIFIER: US 5865965 A

TITLE: Apparatus for electrochemical decontamination of radioactive metallic waste

---------- KWIC ---------

Abstract Text - ABTX (1):

An insulating shield plate (1) divides a room of an electrolysis bath (2) into an anode chamber (13) and a cathode chamber (14). An anode (5) is disposed in the anode chamber (13), and a cathode (6), metallic waste (7) and heater (4) are disposed in the cathode chamber (14). An electrolyte (3) stored in the electrolysis bath (2) flows in a circulation path from a circulating pump (10) through a circulating line (12) and filter (11) to return the electrolysis bath (2). An exhaust gas processing device 9 is connected to the electrolysis bath (2). When a voltage is supplied to the anode (5) and cathode (6), a surface of the metallic waste (7) is charged in a positive polarity to dissolve a base metal of the metallic waste (7). Further, a cylindrical anode (33) is arranged in an electrolyte (32) in an electrolysis bath (31), and a cylindrical metal (34) as a metallic waste is arranged in the cylindrical anode (33). After a bar-shaped cathode (35) is arranged in the cylindrical metal (34), a DC voltage is supplied to the cylindrical anode (33) and the bar-shaped cathode (35). At this time, the system may be constructed in that oxygen occurs by charging in a positive polarity in an inner surface of the cylindrical metal (34) and the base metal of the cylindrical shape is dissolved.

Brief Summary Text - BSTX (19):

an insulating shield plate for dividing a room of the electrolysis bath into an anode chamber and a cathode chamber, and the insulating shield plate which is set in a U-shape along three inner wall surfaces of the electrolysis bath.

Brief Summary Text - BSTX (33):

any one of electrodes of two kinds of the anode and the cathode for electrolysis has a cylindrical shape along the outer shape of the metallic waste having a curved portion, and the other of the electrodes is formed in a bar-shaped in correspondence with an inner shape of the metallic waste.

Brief Summary Text - BSTX (43):

a cylindrical anode which is arranged on an inner wall of the cylindricel insulating shield body;

Brief Summary Text - BSTX (53):

an anode which is arranged at the bottom of the insulating shield vessel;

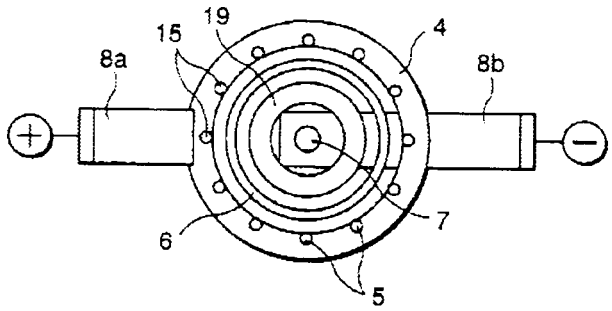


FIG.37A

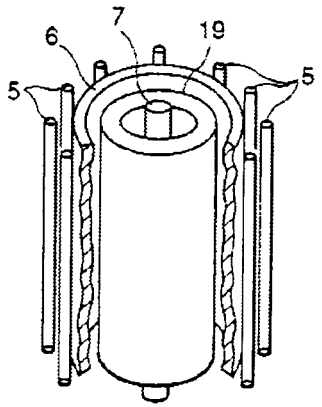


FIG.37B

EAST Browser - L16: (7) 13 and 15 | US 5650053 A | Tag: S | Doc: 3/7 (SORTED) | Format: KWIC

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	Document ID	Pages	1	2	3	4	U	S	C	P	Kind Codes	Sou
1	US 6258251 B1	11										USPAT
2	US 5865965 A	45										USPAT
3	US 5650053 A	13										USPAT
4	US 4352727 A	6										USPAT
5	US 4331527 A	6										USPAT
6	US 3951774 A	5										USPAT
7	US 3929592 A	7										USPAT

US-PAT-NO: 5650053

DOCUMENT-IDENTIFIER: US 5650053 A

TITLE: Electrorefining cell with parallel electrode/concentric cylinder cathode

---------- KWIC ---------

Abstract Text - ABTX (1):

A cathode-anode arrangement for use in an electrolytic cell is adapted for electrochemically refining spent nuclear fuel from a nuclear reactor and recovering purified uranium for further treatment and possible recycling as a fresh blanket or core fuel in a nuclear reactor. The arrangement includes a plurality of inner anodic dissolution baskets that are each attached to a respective support rod, are submerged in a molten lithium halide salt, and are rotationally displaced. An inner hollow cylindrical-shaped cathode is concentrically disposed about the inner anodic dissolution baskets. Concentrically disposed about the inner cathode in a spaced manner are a plurality of outer anodic dissolution baskets, while an outer hollow cylindrical-shaped is disposed about the outer anodic dissolution baskets. Uranium is transported from the anode baskets and deposited in a uniform cylindrical shape on the inner and outer cathode cylinders by rotating the anode baskets within the molten lithium halide salt. Scrapers located on each anode basket abrade and remove the spent fuel deposits on the surfaces of the inner and outer cathode cylinders, with the spent fuel falling to the bottom of the cell for removal. Cell resistance is reduced and uranium deposition rate enhanced by increasing the electrode area and reducing the anode-cathode spacing. Collection efficiency is enhanced by trapping and recovery of uranium dendrites scrapped off of the cylindrical cathodes which may be greater in number than two.

Detailed Description Text - DETX (4):

In accordance with the present invention, concentrically disposed within the outer cathode cylinder 14 is an inner cathode cylinder 12. Each of the outer and inner cathode cylinders 14, 12 is maintained in a fixed position relative to each another and is preferably comprised of a suitable metal which may be a ferrous or a molybdenum alloy, as well known in the art. Disposed intermediate the outer cathode cylinder 14 and the inner cathode cylinder 12 and arranged in a spaced manner about the inner cathode cylinder are a plurality of outer anode baskets 18a-18h. Each of the outer anode baskets 18a-18h is attached to and supported by a respective support rod as shown for the combination of basket support rod 64 and outer anode basket 18h. Disposed within the inner cathode cylinder 12 are a plurality of spaced inner anode baskets 16a-16d. Each of the inner anode baskets 16a-16d is similarly coupled to and supported by a respective support rod within the inner cathode cylinder 12. Each of the aforementioned anode baskets is in the form of an apertured, or porous, container holding a spent nuclear fuel which has been fragmented.

Detailed Description Text - DETX (5):

Also disposed within the inner and outer cathode cylinders 12, 14 is an

United States Patent [19]

Gay et al.

[11] Patent Number: 5,650,053

[45] Date of Patent: Jul. 22, 1997

[54] **ELECTROREFINING CELL WITH PARALLEL ELECTRODE/CONCENTRIC CYLINDER CATHODE**

[75] Inventors: **Eddie C. Gay**, Park Forest; **William E. Miller**, Naperville; **James J. Laidler**, Burr Ridge, all of Ill.

[73] Assignee: **The United States of America as represented by the United States Department of Energy**, Washington, D.C.

[21] Appl. No.: **562,612**

[22] Filed: **Nov. 24, 1995**

[51] **Int. Cl.**[6] **C25D 17/00**; C25C 3/00; A62D 3/00

[52] **U.S. Cl.** **204/212**; 205/44; 205/46; 205/47; 205/49; 204/272; 204/669; 204/671; 204/243 R; 204/215; 204/227; 204/244; 204/287; 588/201; 423/3

[58] **Field of Search** 588/20, 201; 976/DIG. 379, 976/DIG. 380, DIG. 266, DIG. 268; 205/44, 46, 47, 49; 204/272, 669, 671, 212, 222, 243 R, 199, 200, 215, 216, 217, 227, 244, 287, 44, 46, 47, 49

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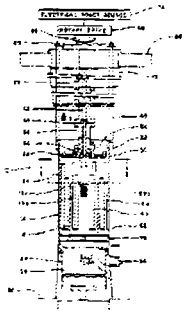
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Primary Examiner—Kathryn L. Gorgos
Assistant Examiner—Alex Noguerola
Attorney, Agent, or Firm—Hugh W. Glenn; Thomas G. Anderson; William R. Moser

[57] **ABSTRACT**

A cathode-anode arrangement for use in an electrolytic cell is adapted for electrochemically refining spent nuclear fuel from a nuclear reactor and recovering purified uranium for further treatment and possible recycling as a fresh blanket or core fuel in a nuclear reactor. The arrangement includes a plurality of inner anodic dissolution baskets that are each attached to a respective support rod, are submerged in a molten lithium halide salt, and are rotationally displaced. An inner hollow cylindrical-shaped cathode is concentrically disposed about the inner anodic dissolution baskets. Concentrically disposed about the inner cathode in a spaced manner are a plurality of outer anodic dissolution baskets, while an outer hollow cylindrical-shaped is disposed about the outer anodic dissolution baskets. Uranium is transported from the anode baskets and deposited in a uniform cylindrical shape on the inner and outer cathode cylinders by rotating the anode baskets within the molten lithium halide salt. Scrapers located on each anode basket abrade and remove the spent fuel deposits on the surfaces of the inner and outer cathode cylinders, with the spent fuel falling to the bottom of the cell for removal. Cell resistance is reduced and uranium deposition rate enhanced by increasing the electrode area and reducing the anode-cathode spacing. Collection efficiency is enhanced by trapping and recovery of uranium dendrites scrapped off of the cylindrical cathodes which may be greater in number than two.

14 Claims, 8 Drawing Sheets



EAST Browser - L16: [7] 13 and 15 | US 4352727 | Tag: S | Doc: 4/7 (SORTED) | "Full" 1/6 (Total images 6)

File Edit View Tools Window Help

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1	US 6258251 B1	11										USPAT
2	US 5865965 A	45										USPAT
3	US 5650053 A	13										USPAT
4	US 4352727 A	6										USPAT
5	US 4331527 A	6										USPAT
6	US 3951774 A	5										USPAT
7	US 3929592 A	7										USPAT

US-PAT-NO: 4352727

DOCUMENT-IDENTIFIER: US 4352727 A
See image for Certificate of Correction

TITLE: Rotogravure cylinder plating and de-plating apparatus

---------- KWIC ----------

Detailed Description Text - DETX (1):

Referring now to the drawings in which like reference numerals denote similar elements, the plating apparatus includes a tank having an end wall 2. A cylinder 4 to be plated is rotatably supported at its ends by bearings 6, in which it is rotatably driven by a suitable power device, not shown. Since the tank and cylinder mounting and drive are conventional, they are not detailed. On each side of the cylinder are disposed concavo-convex baskets 8 and 8a of polypropylene whose concave walls are disposed towards the cylinder. The baskets are suspended by hanger bars 10 attached as at 11 to current-carrying rails 12. The ends of the rails are conventionally supported by the tank ends. The inner walls 16 of the baskets have perforations 18 and the outer sides 20 of the baskets are blind, except for two rows of holes near their tops which permit plating solution to flow through. Suspended within the baskets and against the inner sides of inner walls are lead anodes 24 which consist of curved flat strips 26 attached as at 28 to the anode rail. The upper portions of the lead anode strips 26 are coated to protect them from the electrolyte and the lower portions are bare and in intimate contact with the copper nuggets 34. Mounted along the lower inner wall of basket 8 is a manifold 36, which is less than 180.degree. away from the top of the cylinder and which is provided with jet outlets 38 which inject electrolyte 40 between the basket and cylinder and in the direction of basket rotation. Electrolyte 40 consisting of 220-250 g/liter copper sulphate and 60 g/liter sulfuric acid fills the tank to a level 42. High phosphor copper mini-nuggets 46, preferably 0.04 to 0.06 percent phosphor, are used. Plastic shield plates 48 are used when cylinders of shorter length are plated so as to prevent over-plating at the cylinder ends.

Current US Cross Reference Classification - CCXR (2):

204/272

United States Patent [19]

Metzger

[11] **4,352,727**

[45] * **Oct. 5, 1982**

[54] **ROTOGRAVURE CYLINDER PLATING AND DE-PLATING APPARATUS**

[75] Inventor: **Hubert Metzger, Milwaukee, Wis.**

[73] Assignee: **Printing Machinery & Electronics Corporation, Inc., Milwaukee, Wis.**

[*] Notice: The portion of the term of this patent subsequent to Oct. 5, 1999, has been disclaimed.

[21] Appl. No.: **255,281**

[22] Filed: **Apr. 17, 1981**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 211,562, Dec. 1, 1980.

[51] Int. Cl.³ C25D 17/00; C25D 17/12

[52] U.S. Cl. 204/212; 204/25; 204/272; 204/285

[58] Field of Search 204/212, 285, 25, 272, 204/275

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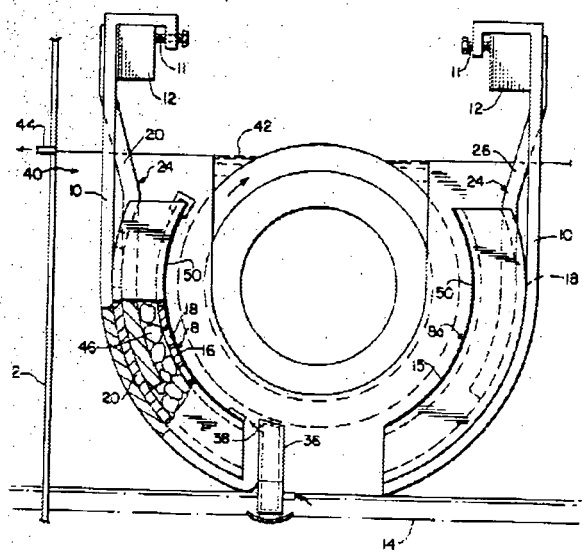
Primary Examiner—T. M. Tufariello
Attorney, Agent, or Firm—Littlepage & Webner

[57] **ABSTRACT**

Polypropylene plastic baskets for phosphorized or non-phosphorized copper anode nuggets are suspended, one on each side of a cylinder to be plated, in a bath of plating electrolyte. The tops of the baskets are disposed beneath the surface of the plating solution, the upper portion of the cylinder is above the surface of the electrolyte, lead anode conductor strips extend downwardly along the insides of the rear walls of the baskets, and the front walls of the baskets are perforated.

When the cylinder is printed out, it is returned to the plating apparatus and reversably plated so as to return the copper to the nuggets. In order to prevent the copper from building up through the perforations in the inner walls of the baskets, a porous plastic sheet is disposed over the inner surface of the inner walls of the baskets.

6 Claims, 2 Drawing Figures



EAST Browser - L16: (7) 13 and 15 | US 4331527 | Tag: S | Doc: 5/7 (SORTED) | "Full" 1/6 (Total images 6)

File Edit View Tools Window Help

	Document ID	Pages	1	2	3	4	5	6	S	C	P	Kind Codes	Sou
1	US 6258251 B1	11											USPAT
2	US 5865965 A	45											USPAT
3	US 5650053 A	13											USPAT
4	US 4352727 A	6											USPAT
5	US 4331527 A	6											USPAT
6	US 3951774 A	5											USPAT
7	US 3929592 A	7											USPAT

US-PAT-NO: 4331527

DOCUMENT-IDENTIFIER: US 4331527 A
See image for Certificate of Correction

TITLE: Rotogravure cylinder plating apparatus

---------- KWIC ---------

Detailed Description Text - DETX (1):

Referring now to the drawings in which like reference numerals denote similar elements, the plating apparatus includes a tank having an end wall 2. A cylinder 4 to be plated is rotatably supported at its ends by bearings 6, in which it is rotatably driven by a suitable power device, not shown. Since the tank and cylinder mounting and drive are conventional, they are not detailed. On each side of the cylinder are disposed concave-convex baskets 8 and 8a of polypropylene whose concave walls are disposed towards the cylinder. The baskets are suspended by hanger bars 10 attached as at 11 to anode current-carrying rails 12. The ends of the anode rails are conventionally supported by the tank ends. The inner walls 16 of the baskets have perforations 18 and the outer sides 20 of the baskets are blind, except for two rows of holes near their tops which permit plating solution to flow through. Suspended within the baskets and against the inner sides of outer walls are lead anodes 24 which consist of curved flat strips 26 attached as a 28 to the anode rail. The upper portions of the lead anode strips 26 are coated to protect them from the electrolyte and the lower portions are bare and in intimate contact with the copper nuggets 34. Mounted along the lower inner wall of basket 8 is a manifold 36, which is less than 180.degree. away from the top of the cylinder and which is provided with jet outlets 38 which inject electrolyte 40 between the basket and cylinder and in the direction of basket rotation. Electrolyte 40 consisting of 220-250 g/liter copper sulphate and 60 g/liter sulfuric acid fills the tank to a level 42. The level 42 is maintained, as by an overflow return 44. High phosphor copper mini-nuggets 46, preferably 0.04 to 0.06 percent phosphor, are used. Plastic shield plates 48 are used when cylinders of shorter length are plated so as to prevent over-plating at the cylinder ends.

Claims Text - CLTX (3):

elongate metalic anode strips having upper protectively coated portions disposed above the baskets, and lower bare portions extending downwardly along inner sides of the outer basket walls, said lower portion being arcuate and concentric with the cylinder,

Current US Cross Reference Classification - CCXR (1):

204/272

United States Patent [19]

Metzger

[11] **4,331,527**

[45] **May 25, 1982**

[54] **ROTOGRAVURE CYLINDER PLATING APPARATUS**

[75] Inventor: **Hubert Metzger, Brookfield, Wis.**

[73] Assignee: **Printing Machinery & Electronics, Inc., Milwaukee, Wis.**

[21] Appl. No.: **211,562**

[22] Filed: **Dec. 1, 1980**

[51] Int. Cl.³ C25D 17/00; C25D 17/12

[52] U.S. Cl. 204/212; 204/25; 204/272; 204/285

[58] Field of Search 204/212, 285, 25, 272, 204/275

[56] **References Cited**

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FOREIGN PATENT DOCUMENTS

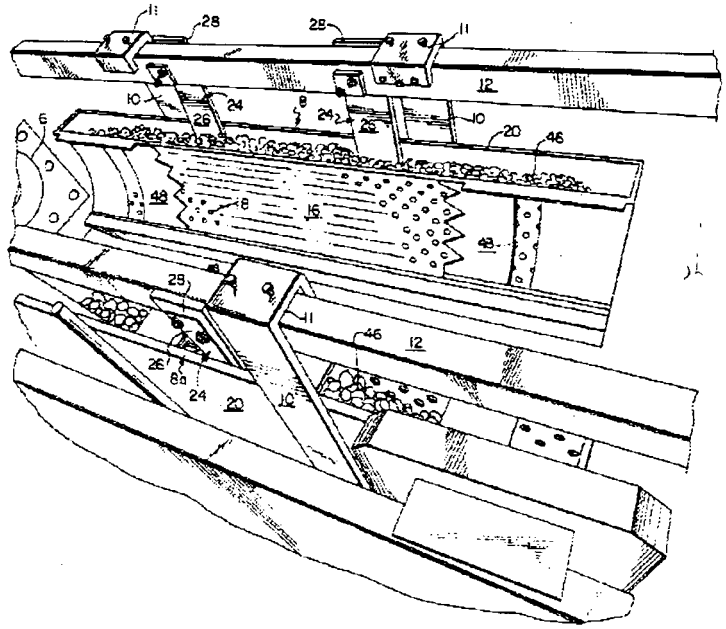
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Primary Examiner—T. Tufariello
Attorney, Agent, or Firm—Littlepage & Webner

[57] **ABSTRACT**

Polypropylene plastic baskets for phosphor copper anode nuggets are suspended, one on each side of a cylinder to be plated, in a bath of plating electrolyte. The tops of the baskets are disposed beneath the surface of the plating solution, the upper portion of the cylinder is above the surface of the electrolyte, and lead anode conductor strips extend downwardly along the insides of the rear walls of the baskets.

4 Claims, 2 Drawing Figures



EAST Browser - L16: (7) 13 and 15 | US 3929592 | Tag: S | Doc: 7/7 (SORTED) | "Full" 2/7 (Total images 7)

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	Document ID	Pages	1	2	3	4	U	S	C	P	Kind Codes	Sou
2	US 5865965 A	45										USPAT
3	US 5650053 A	13										USPAT
4	US 4352727 A	6										USPAT
5	US 4331527 A	6										USPAT
6	US 3951774 A	5										USPAT
	US 3929592 A	7										USPAT

US-PAT-NO: 3929592

DOCUMENT-IDENTIFIER: US 3929592 A

TITLE: Plating apparatus and method for rotary engine housings

---------- KWIC ----------

Detailed Description Text - DETX (8):

The portion of the anode above passageway 22 in contact with the electroplating solution has a nonconductive coating 48. The portion of anode 42 in passageway 22, directly opposite the metal plates and the working surfaces of the housings, has a plurality of holes 50 radially arrayed throughout its length that communicate the anode interior with passageway 22. The holes 50 are approximately 1/8 - 1/4 inch in diameter and are positioned about 1 inch apart radially around the periphery of the anode and alternately spaced axially in rows about 1/2 inch apart. Both sides of the anode at its minor transverse dimension, or waist portion, are shielded with a plastic strip 52 and 52' about 11/4 inch wide along the entire length of the passageway 22. Strip 52 serves as a shield and is only wide enough to maintain a generally constant ratio of anode-to-cathode area radially around the anode. The minor dimension, or waist, portions of the housing working surfaces are thus prevented from plating at a faster rate than the balance of the housing working surfaces.

Claims Text - CLTX (7):

an insoluble anode having a generally epitrochoidal transverse outer periphery and an interior space, said anode coaxially extending throughout said passageway parallel to and radially spaced inwardly from said aligned inner surfaces,

Claims Text - CLTX (17):

an insoluble anode having a generally epitrochoidal transverse outer periphery and an interior space, said anode coaxially extending throughout said passageway parallel to and radially spaced inwardly from said aligned inner surfaces,

Claims Text - CLTX (34):

a vertical tubular insoluble anode having an epitrochoidal horizontal outer periphery concentric with and smaller than said nonconductive plate openings coaxially disposed in said housing passageway and uniformly radially spaced inwardly from said aligned inner surfaces, the radial spacing between said anode and said passageway being about two to three times greater than the radial spacing from said nonconductive plates,

Current US Cross Reference Classification - CCXR (2):

U.S. Patent Dec. 30, 1975 3,929,592

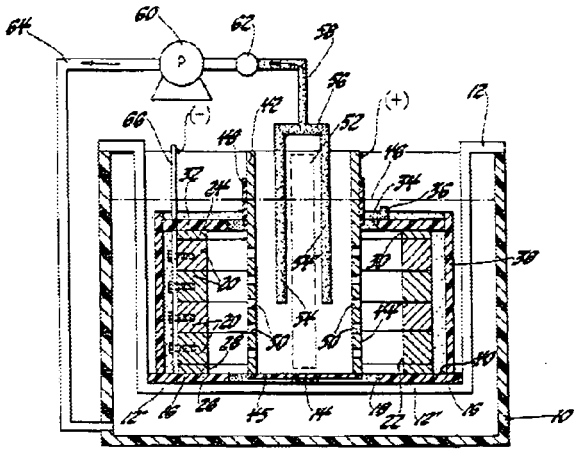


Fig. 1

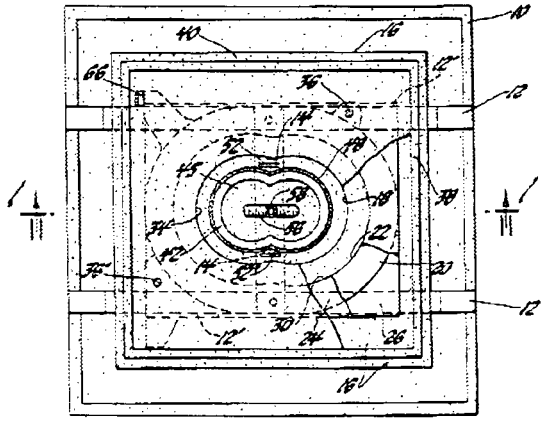


Fig. 2

EAST Browser - [18: (96) 13 and 16 | US 6103076 A | Tag: S | Doc: 10/96 (SORTED) | Format : KWIC

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	Document ID	Pages	1	2	3	4	U	S	C	P	Kind Codes	Sou
5	US 6248221 B1	18						☑				USPAT
6	US 6224721 B1	9						☑				USPAT
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9	US 6117285 A	32						☑				USPAT
10	US 6103076 A	19						☑				USPAT
11	US 6007686 A	23						☑				USPAT

US-PAT-NO: 6103076

DOCUMENT-IDENTIFIER: US 6103076 A

TITLE: Auxiliary anode element suitable for use in electroplating a bent tubular workpiece

---------- KWIC ---------

Brief Summary Text - BSTX (5):

In electroplating, generally, an anode element and a workpiece to be electroplated are immersed in a plating liquid containing plating metal ions. Electric current is supplied between the anode element and the workpiece serving as a cathode element so that the workpiece is electroplated. When the workpiece is tubular, the inside of the workpiece is concealed from the anode element such that a sufficient amount of current flow for the plating is not obtained inside the tubular workpiece. Accordingly, an inner surface of the tubular workpiece has an extremely low degree of plating relative to an outer surface thereof.

Detailed Description Text - DETX (13):

Upon completion of the racking, the filler pipe 1 suspended from the hanger 5 is carried along the line so that the above-described preparation steps including degreasing, cleaning, etc. are sequentially executed. Upon completion of the preparation steps, the filler pipe 1 is transferred to the galvanizing step. The filler pipe 1, suspended from the hanger 5, is immersed in the plating liquid 31 contained in the plating bath 30. The cathode bar 12 connected to the cathode side frame 6 is further connected to the cathode of the power supply system, whereas the anode side frame 1 is connected via the contact piece 18 to the anode of the power supply system. As a result, an electric current is caused to flow from the zinc plates 32 and the metal wire 21 both connected to the anode to the filler pipe 1 connected to the cathode, whereupon the outer and inner surfaces of the filler pipe 1 is galvanized. The galvanizing step is executed for twenty and several minutes.

Detailed Description Text - DETX (15):

According to the foregoing embodiment, the auxiliary anode element 20 is inserted into the filler pipe 1 when the filler pipe 1 having the vent portions is galvanized. Consequently, the inner surface of the filler pipe 1 can sufficiently be galvanized as well as the outer surface thereof. More specifically, since the metal wire 21 is flexible, the metal wire, bent according to the bent form of the filler pipe 1, is inserted into the filler pipe 1. Furthermore, since the insulating spacers 22 are fitted with the filler pipe 1, the metal wire 21 can be prevented from coming into direct contact with the inner surface of the filler pipe. Consequently, the current flow distribution in the hollow interior of the filler pipe 1 is improved such that a sufficient plating (plated coating) thickness can be obtained. Furthermore, the inner surface of the filler pipe 1 can sufficiently be galvanized without non-plated portions due to the contact of the metal wire 21 with the inner surface of the filler pipe 1. The inventor of the present invention has confirmed that the same coating thickness by the plating can be

United States Patent [19]

Mizuno

[11] Patent Number: 6,103,076

[45] Date of Patent: Aug. 15, 2000

[54] AUXILIARY ANODE ELEMENT SUITABLE FOR USE IN ELECTROPLATING A BENT TUBULAR WORKPIECE

[75] Inventor: Chikanori Mizuno, Nagoya, Japan

[73] Assignee: Daiwa Excel Co., Ltd., Aichi, Japan

[21] Appl. No.: 09/066,680

[22] Filed: Apr. 28, 1998

[30] Foreign Application Priority Data

Apr. 30, 1997 [JP] Japan 9-112911

[51] Int. Cl.[7] C25D 17/12

[52] U.S. Cl. 204/286; 204/272; 204/280; 204/288; 205/131

[58] Field of Search 205/131; 204/272, 204/280, 286, 288

[56] References Cited

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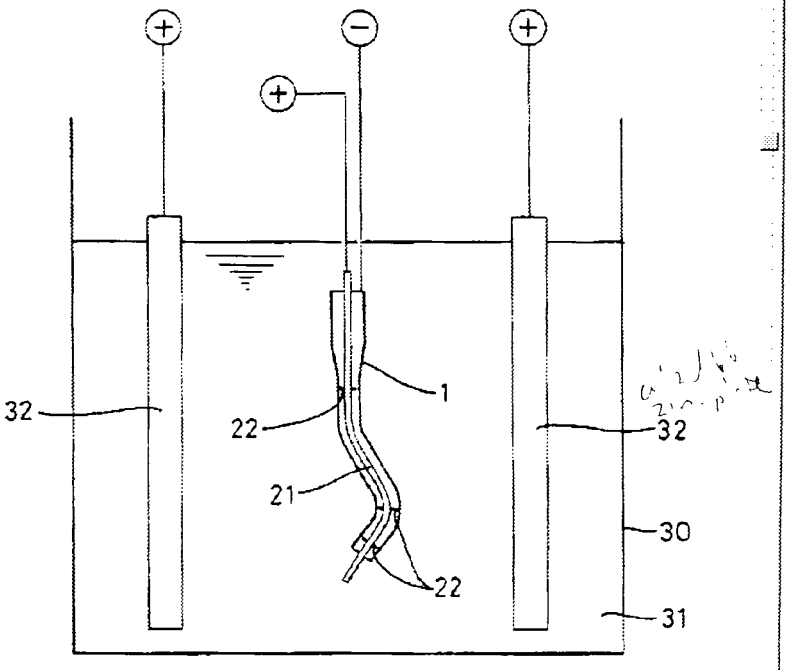
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Primary Examiner—Kathryn Gorgos
Assistant Examiner—William T. Leader
Attorney, Agent, or Firm—Wenderoth, Lind & Ponack, L.L.P.

[57] ABSTRACT

A flexible auxiliary anode element for electroplating a tubular workpiece while the workpiece and an anode element are immersed in a plating liquid contained in a plating both. The flexible auxiliary anode element can be inserted into a hollow interior of the workpiece so that a metal wire of the auxiliary anode element is insulated from an inner peripheral surface of the workpiece by an insulating spacer.

9 Claims, 14 Drawing Sheets



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	Document ID	Pages	1	2	3		4	U	S	C	P	Kind Codes	Sou
27	US 4238300 A	4							☑				USPAT
28	US 4212708 A	5							☑				USPAT
29	US 4192723 A	6							☑				USPAT
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31	US 4055591 A	10						☑					USPAT
32	US 4012294 A	16						☑					USPAT
33	US 3990954 A	3						☑					USPAT

Brief Summary Text - BSTX (17):

The operating conditions of the present method are not critical. It is possible to work at room temperature and use, for instance, a concentrated HAuCl.sub.4 solution (about 80-100 g/l of gold) to which concentrated aqueous ammonia (about 30%) is added slowly. Practice has however shown that it is advantageous to use a very concentrated HAuCl.sub.4 solution (more than 500 g/l) with very little free HCl. After adding an excess of ammonia until the precipitation is complete, the precipitate is allowed to settle for decantation. Then the supernatant liquid is removed by syphoning and replaced by pure water. The precipitate is agitated, decantation is carried out again and this washing step is repeated 2 or 3 times until practically all chloride has been eliminated. Washing by filtration should preferably be avoided for fear of drying up of the precipitate (explosion hazard). Then, after eliminating finally, as well as possible, the rinsing waters, an aqueous solution of ammonium sulfite (commercial grade is suitable) is added for dissolving the precipitate. The quantity and concentration of the sulfite solution is calculated to ensure that the finished ammonium-gold-sulfite solution will contain about 100 g/l of gold for about 160-210 g/l of total ammonium sulfite . These values are, in fact, not at all critical but it is preferable to keep as close as possible thereto for convenience when using, thereafter, the obtained ammonium-gold-sulfite solution for preparing or maintaining gold plating baths.

Brief Summary Text - BSTX (18):

The aqueous electrolytic bath containing the present ammonium-gold-sulfite complex which is prepared from the above discussed solution is stable and is operated within the 6-8 pH range. It comprises 1 to 50 g/l of gold metal, 10-400 g/l of ammonium sulfite. 10 to 400 g/l of buffering and conducting salts and it may or not further comprise alloying metals in the form of water-soluble compounds or complexes.

Brief Summary Text - BSTX (19):

Thus, this bath which contains the gold in the form of an ammonium-gold-sulfite complex is able to provide electrodeposits in acidic media as well as alloyed gold and pure gold, and without needing depolarizers such as arsenic or selenium, even at current densities of 0.25 to 0.5 A/dm.sup.2, or stabilizers such as polyamines, which was practically impossible with alkali-gold-sulfite baths of the prior art. Under such conditions, it is possible with the present bath to obtain bright and semi-bright 24 karat deposits, homogeneous and non-porous. Further, because of the absence of arsenic, this bath is acceptable in the countries in which the use of this element in industry is restricted or prohibited by law.

Brief Summary Text - BSTX (20):

Moreover, this bath being adaptable to acid pH, it is perfectly suited to the deposition of lower karat gold alloys, e.g., 15 to 18 karat. As alloying metals for instance Cd, Pd, Cu, Zn, Sb, In, Ni, Co, Fe, Pb, Bi, Ru, etc., can be mentioned with no limitation. The concentration of those metals in the bath can be e.g. 0.01-150 g/l. These metals are present in the bath as their salts or complexes conventionally used in gold baths, e.g., the sulfates, nitrites, sulfamates, phosphates, pyrophosphates, acetates, citrates, phosphorates

obtain lower karat gold-alloys deposits. Similarly, Swiss Pat. No. 534,215 discloses an alkali-sulfite gold bath (sodium or potassium) for the electrolytic deposition of gold-palladium alloys in which there is added, for stabilization at pH slightly below 7, aliphatic, cycloaliphatic and heterocyclic amines.

However, gold baths prepared in the above described manner have the following disadvantages: during electrolysis of the bath, the stabilizing amines which enable the latter to operate at pH below 7 are progressively liberated as gold is removed for plating from the complex and as the bath is replenished with gold and stabilizers. Further, these amines are oxidized and decomposed at the anode and, either themselves, or their degradation products impede the operation of the bath, for example by complexing and blocking the common metals which must co-deposit with the gold in the plated alloy and, thus, decreasing the useful concentration thereof at the cathode. Consequently, these baths have a very short working life and must be frequently renewed.

It should be moreover remarked that in U.S. Pat. No. 3,787,463, it is mentioned that polyamine A can also consist of ammonia. However, the present Applicants have not succeeded in preparing such a compound of Au^{3+} wherein A represents NH_3 and, simultaneously, ME represents NH_4^+. Thus, in contrast to what happens with amines, when ammonium hydroxide is added to a solution of trivalent gold chloride, the mixture precipitates before the introduction of the sulfite. This precipitate, the nature of which is ill-determined, is called "fulminating gold" in the chemical literature (see the heretofore mentioned reference: PASCAL, p. 783). It is interesting to note that the method of the invention is precisely based on this precipitation phenomenon and provides an ammonium-gold-sulfite complex solution which permits, by means of the gold bath prepared therefrom, one to remedy most of the above mentioned disadvantages.

Thus, the method of the invention for the preparation of an aqueous solution of a sulfite complex of monovalent gold and ammonium comprises treating an aurihydrochloric acid ($HAuCl_4$) aqueous solution with ammonia which provides a precipitate of a gold compound, then decanting the supernatant solution and washing the precipitate, by decantation, until practically all chloride ions are eliminated, then adding to the moist precipitate a sufficient quantity of an ammonium sulfite solution for dissolving the precipitate and ensuring the reduction of trivalent gold in monovalent gold.

The complete reduction of trivalent gold into monovalent gold can be easily checked by electrolyzing a sample of the above-mentioned solution. When a yield approaching 100% (120 mg/Amp×min) is reached, the reduction is complete. Thus, at least 3.5 equivalent of sulfite (3.5 moles) of ammonium sulfite per mole of precipitated gold (calculated on the number of moles of starting $HAuCl_4$) will preferably be used.

This process of preparation of a solution of gold-sulfite complex is particularly economical as compared to older processes. Thus, the precipitation of gold with ammonia is substantially quantitative and the precipitate is easily washable by simple decantation as its particles will settle relatively rapidly at the bottom of the container used. The exact nature of this precipitate has not been investigated. Presumably, it is similar to the "fulminating" gold compounds reported by DUMAS, RASCHIG and other workers (see PASCAL, op. cit.),

maybe in admixture with hydroxides $Au(OH_3)$. The specific chemical formula and the exact nature of the gold-sulfite complex which is obtainable in solution by the present method has never been determined. It is however, probable that it is not similar to the products mentioned in the prior-art (see PASCAL, op. cit. p. 732) since its solution is perfectly stable in water even at slightly acid pH, in contrast to the reports on the ammonium gold-sulfite of formula $(H_4N)_3[Au(SO_3)_2].1\ H_2O$. This stability property was indeed absolutely unexpected and constitutes a surprising factor of the present invention.

The operating conditions of the present method are not critical. It is possible to work at room temperature and use, for instance, a concentrated $HAuCl_4$ solution (about 80–100 g/l of gold) to which concentrated aqueous ammonia (about 30%) is added slowly. Practice has however shown that it is advantageous to use a very concentrated $HAuCl_4$ solution (more than 500 g/l) with very little free HCl. After adding an excess of ammonia until the precipitation is complete, the precipitate is allowed to settle for decantation. Then the supernatant liquid is removed by syphoning and replaced by pure water. The precipitate is agitated, decantation is carried out again and this washing step is repeated 2 or 3 times until practically all chloride has been eliminated. Washing by filtration should preferably be avoided for fear of drying up of the precipitate (explosion hazard). Then, after eliminating finally, as well as possible, the rinsing waters, an aqueous solution of ammonium sulfite (commercial grade is suitable) is added for dissolving the precipitate. The quantity and concentration of the sulfite solution is calculated to ensure that the finished ammonium-gold-sulfite solution will contain about 100 g/l of gold for about 160–210 g/l of total ammonium sulfite. These values are, in fact, not at all critical but it is preferable to keep as close as possible thereto for convenience when using, thereafter, the obtained ammonium-gold-sulfite solution for preparing or maintaining gold plating baths.

The aqueous electrolytic bath containing the present ammonium-gold-sulfite complex which is prepared from the above discussed solution is stable and is operated within the 6–8 pH range. It comprises 1 to 50 g/l of gold metal, 10–400 g/l of ammonium sulfite, 10 to 400 g/l of buffering and conducting salts and it may or not further comprise alloying metals in the form of water-soluble compounds or complexes.

Thus, this bath which contains the gold in the form of an ammonium-gold-sulfite complex is able to provide electrodeposits in acidic media as well as alloyed gold and pure gold, and without needing depolarizers such as arsenic or selenium, even at current densities of 0.25 to 0.5 A/dm^2, or stabilizers such as polyamines, which was practically impossible with alkali-gold-sulfite baths of the prior art. Under such conditions, it is possible with the present bath to obtain bright and semi-bright 24 karat deposits, homogeneous and non-porous. Further, because of the absence of arsenic, this bath is acceptable in the countries in which the use of this element in industry is restricted or prohibited by law.

Moreover, this bath being adaptable to acid pH, it is perfectly suited to the deposition of lower karat gold alloys, e.g., 15 to 18 karat. As alloying metals for instance Cd, Pd, Cu, Zn, Sb, In, Ni, Co, Fe, Pb, Bi, Ru, etc., can be mentioned with no limitation. The concentration of those metals in the bath can be e.g. 0.01–150 g/l. These metals are present in the bath as their salts or

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27	US 4238300 A	4										USPAT
28	US 4212708 A	5										USPAT
29	US 4192723 A	6										USPAT

Brief Summary Text - BSTX (8):

Most widely employed gold -plating electrolytes are based on disulphitoaurats, ethylenediaminodisulphitoaurate and diaminodisulphitoaurate of alkali metals; properties of these gold -plating electrolytes depend on the method of preparing same. This method comprises conversion of aurichlorchydric acid to a sparingly soluble gold compound, auric hydroxide or auric ammoniate to purify from Cl.sup.- ions; this gold compound is treated with solutions of sulphites of alkali metals, followed by stabilization of the resulting sulphite complexes in the solution.

Brief Summary Text - BSTX (9):

The thus-produced sparingly soluble gold compounds are low-stable thus causing a partial evolution of metal gold which, in turn, lowers the desired product yield. This also hinders preparation of highly-concentrated electrolytes for gold -plating which would be stable in storage and use, whereby the efficiency of the gold -plating process is educed.

Brief Summary Text - BSTX (10):

Known in the art is a gold -plating electrolyte (cf. U.S. Pat. No.3,553,896) based on potassium disulphitaurate and having the following composition:

Brief Summary Text - BSTX (11):

K.sub.3 [Au(SO.sub.3).sub.2] : 6.8-68

Brief Summary Text - BSTX (17):

This gold -plating electrolyte has a throwing power of up to 90%, yield current up to 70-80%, period of storage at the temperature of 25.degree.0 C. as long as 4 months, starting point of decomposition at D.sub.k above 0.8 A/dm.sup.2.

Brief Summary Text - BSTX (19):

The process for the preparation of this electrolyte comprises treatment of aurichlorohydric acid with a solution of ammonia at a pH of from 3 to 6 to give basic auric ammoniate, followed by decantation of the mother liquor and washing in hot water. The resulting suspension is added to a hot solution of potassium sulphite (to the concentration of 150 g/l), followed by heat-treatment of the resulting mixture at a temperature ranging from 70.degree. to 90.degree. C. for a period of from 48 to 72 hours and addition of an alkali metal salt of ethylenediaminetetracetic acid, potassium sulphate and potassium hydrogen phosphate. The resulting eletrolyte is filtered-off to recover partly precipitated metallic gold . The yield of the thus-produced gold -plating electrolyte is 30 to 60% as calculated for metal gold .

Brief Summary Text - BSTX (20):

This prior art gold-plating electrolyte has a reduced stability in storage

I

GOLD-PLATING ELECTROLYTE

The present invention relates to the preparation of gold compounds and, more specifically, it relates to a gold-plating electrolyte.

FIELD OF THE INVENTION

The present invention is useful in the preparation of gold reactants for electronics, watch making, jewelry and radio-engineering.

BACKGROUND OF THE INVENTION

Known in the art are gold-plating electrolytes based on sodium or potassium dicyanoaurate and containing also potassium sulphate, potassium hydrogen phosphate, an alkali metal salt of ethylenediaminoacetic acid which are prepared by anodic or chemical dissolution of gold in solutions of alkali metal cyanides.

Preparation and use of this type electrolytes are associated with evolution of toxic compounds and the necessity of making them harmless. Said prior art electrolytes make it possible to obtain a good-quality coating only at large thicknesses thereof.

Preparation and use of said prior art gold-plating electrolytes is also accompanied by difficulties encountered in recovery of gold from spent and mother liquors and outgassing of toxic compounds.

Most widely employed gold-plating electrolytes are based on disulphitoaurate, ethylenediaminodisulphitoaurate and diaminodisulphitoaurate of alkali metals; properties of these gold-plating electrolytes depend on the method of preparing same. This method comprises conversion of aurichlorohydric acid to a sparingly soluble gold compound, auric hydroxide or auric ammoniate to purify from Cl⁻ ions; this gold compound is treated with solutions of sulphites of alkali metals, followed by stabilization of the resulting sulphite complexes in the solution.

The thus-produced sparingly soluble gold compounds are low-stable thus causing a partial evolution of metal gold which, in turn, lowers the desired product yield. This also hinders preparation of highly-concentrated electrolytes for gold-plating which would be stable in storage and use, whereby the efficiency of the gold-plating process is educed.

Known in the art is a gold-plating electrolyte (cf. U.S. Pat. No.3,893,896) based on potassium disulphitaurate and having the following composition:

$K_3[Au(SO_3)_2]$: 6.8-68
Na_2H_2Edta: 0.1-100
K_2SO_4: 1.0-100
K_2HPO_4: 10-40
water: the balance

(current density is $D_k = 0.1$-1.2 A/dm²; T = 18°-80° C.).

This gold-plating electrolyte has a throwing power of up to 90%, yield current up to 70-80%, period of storage at the temperature of 25°0 C. as long as 4 months, starting point of decomposition at D_k above 0.8 A/dm².

This electrolyte ensures the manufacture of high-quality fine coatings with Vickers hardness of from 80 to 220 kg/mm², porosity of from 25 to 30 pores/cm² at the thickness of 15 mcm and non-porous at a thickness of below 5 mcm.

The process for the preparation of this electrolyte comprises treatment of aurichlorohydric acid with a solution of ammonia at a pH of from 3 to 6 to give basic auric ammoniate, followed by decantation of the mother liquor and washing in hot water. The resulting suspension is added to a hot solution of potassium sulphite (to the concentration of 150 g/l), followed by heat-treatment of the resulting mixture at a temperature ranging from 70° to 90° C. for a period of from 48 to 72 hours and addition of an alkali metal salt of ethylenediaminetetracetic acid, potassium sulphate and potassium hydrogen phosphate. The resulting eletrolyte is filtered-off to recover partly precipitated metallic gold. The yield of the thus-produced gold-plating electrolyte is 30 to 60% as calculated for metal gold.

This prior art gold-plating electrolyte has a reduced stability in storage and use, as well as insufficient technological parameters.

SUMMARY OF THE INVENTION

It is the main object of the present invention to provide a gold-plating electrolyte possessing improved technological parameters and a high stability in storage and use.

This object is accomplished by that a gold-plating electrolyte which contains a complex gold compound with sulphite-ion, an alkali metal salt of ethylenediaminetetracetic acid, potassium hydrogen phosphate, potassium sulphate and water, in accordance with the present invention contains, as the complex gold compound with sulphite-ion, hexapotassium μ-ethylenediaminetetracetate bis(gold sulphite /I/) with the following proportions of the components (g/l):

- hexapotassium μ-ethylenediaminetetracetate bis(gold sulphite /I/): 10.5–123.0
- an alkali metal salt of ethylenediaminetetracetic acid: 17.8–140.0
- potassium sulphate: 12.6–110.0
- potassium hydrogen phosphate: 4.7–40.0
- water: the balance

Quantitative content of the components in the electrolyte is determined by that at a content of hexapotassium μ-ethylenediaminotetracetate bis(aurous sulphite) below 10.5 g/l, the rate of electrodeposition is insufficient, while at a content thereof above 123 g/l the quality of coatings is impaired. Proportions of the alkali metal salt of ethylenediaminetetracetic acid, potassium sulphate and potassium hydrogen phosphate affect the quality of coatings, in particular hardness thereof; these properties are defined by the content of hexapotassium μ-ethylenediaminetetracetate bis(aurous sulphite).

It is advisable that the gold-plating electrolyte according to the present invention contain the components in the following proportions, g/l:

- hexapotassium μ-ethylenediaminetetracetate bis(aurous sulphite): 10.5–25.0
- disodium-dipotassium salt of ethylenediaminetetracetic acid: 17.8–40.0
- potassium sulphate: 12.6–28.4
- potassium hydrogen phosphate: 4.7–10.4
- water: the balance

The above-specified amounts of the components of the optimal gold-plating electrolyte composition ensure a maximum reliability thereof in use. Thus, K_3Na_2Edta in said amounts inhibits dissociation of ethylenediaminetetracetateion $K_3[Au(SO_3)_2Edta]$ under the effect of the electric field forces in the layer adjacent to the electrode. In this case the electrochemical reaction proceeds only in a double electric layer and prevents spontaneous decomposition of the complex within the solution volume accompanied by liberation of gold in the powder-like form. K_2SO_4 in the above-

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13	US 5277790 A	6						☑				USPAT
14	US 5266183 A	4					☑					USPAT

US-PAT-NO: 5277790

DOCUMENT-IDENTIFIER: US 5277790 A

TITLE: Non-cyanide electroplating solution for gold or alloys thereof

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Abstract Text - ABTX (1):

Disclosed are cyanide free electroplating solutions for gold or alloys thereof; said solutions comprising gold in the form of a soluble sulfite complex, an added source of sulfite and/or bisulfite ion and a supporting electrolyte; and said solutions further comprising both an organic polyamine or mixture of polyamines of molecular weight from about 60 to 50,000, and an aromatic organic nitro compound; wherein the pH of said solutions is below about 6.5.

TITLE - TI (1):

Non-cyanide electroplating solution for gold or alloys thereof

Brief Summary Text - BSTX (2):

Electroplating solutions containing gold in the form of a soluble sulfite complex have been known since about 1962, see, e.g., Smith, U.S. Pat. No. 3,0059,789. As originally formulated, commercial solutions based on a gold-sulfite complex were stable only at pH values above about 8.0, and in practice were usually operated at pH range of from 9 to 11. In 1969, Meyer et al., in Swiss Patent No. 506,828, reported that in the presence of organic polyamines, notably ethylenediamine, sulfite -based plating solutions for gold -copper alloys could be stabilized at pH values as low as 6.5. More recently, Kikuchi et al., in the 1990 Japanese Kokai Tokkyo Koho JP 02,232,378 (90,232,378), reported a solution containing sodium gold sulfite which was stabilized at pH 8 by the presence of sodium 3-nitrobenzene sulfonate.

Brief Summary Text - BSTX (3):

Other gold sulfite complex plating compositions include the following:

Brief Summary Text - BSTX (4):

Smith et al., U.S. Pat. No. 3,057,789, which discloses a cyanide free electrolytic bath containing a potassium or a sodium gold sulfite complex and disodium ethylenediamine tetracetate.

Brief Summary Text - BSTX (5):

Smith et al., U.S. Pat. No. 3,666,640, entitled "Gold Plating Bath and Process," which discloses an aqueous beth for electroplating gold, comprising;

NON-CYANIDE ELECTROPLATING SOLUTION FOR GOLD OR ALLOYS THEREOF

BACKGROUND OF THE INVENTION

Electroplating solutions containing gold in the form of a soluble sulfite complex have been known since about 1962, see, e.g., Smith, U.S. Pat. No. 3,0059,789. As originally formulated, commercial solutions based on a gold-sulfite complex were stable only at pH values above about 8.0, and in practice were usually operated at pH range of from 9 to 11. In 1969, Meyer et al., in Swiss Patent No. 506,828, reported that in the presence of organic polyamines, notably ethylenediamine, sulfite-based plating solutions for gold-copper alloys could be stabilized at pH values as low as 6.5. More recently, Kikuchi et al., in the 1990 Japanese Kokai Tokkyo Koho JP 02,232,378 (90,232,378), reported a solution containing sodium gold sulfite which was stabilized at pH 8 by the presence of sodium 3-nitrobenzene sulfonate.

Other gold-sulfite complex plating compositions include the following:

Smith et al., U.S. Pat. No. 3,057,789, which discloses a cyanide free electrolytic bath containing a potassium or a sodium gold sulfite complex and disodium ethylenediamine tetracetate.

Smith et al., U.S. Pat. No. 3,666,640, entitled "Gold Plating Bath and Process," which discloses an aqueous bath for electroplating gold, comprising; alkali gold sulfite; an alkali sulfite; an alkali sulfate; a soluble compound of cadmium, copper, nickel, and/or arsenic; and an organic acid chelating agent, wherein the bath contains sufficient acid or alkali to adjust its pH to between 8.5 to 13.

Stevens, U.S. Pat. No. 4,048,023, which discloses a slightly alkaline gold plating solution, free of cyanide and phosphates, containing a sodium gold sulfite complex and a palladosamine chloride complex.

Laude et al., U.S. Pat. No. 4,192,723, which provides an aqueous solution comprising monovalent gold and ammonium sulfite complex.

Wilkinson, U.S. Pat. No. 4,366,035, which described a cyanide-free bath for the electrodeposition of gold alloys comprising an aqueous alkaline mixture of a gold sulfite, a water soluble copper alloying salt or complex, a water soluble palladium alloying salt or complex and an alkali metal sulfite or ammonium sulfite.

Baker et al., U.S. Pat. No. 4,435,253, which provides gold sulfite electroplating solutions comprising an alkali metal or ammonium gold sulfite, a water soluble salt of thallium metal, and a non-hydroxy, non-amino carboxylic acid.

Shemyakina et al., U.S. Pat. No. 4,497,696, which relates to a gold plating electrolyte which comprises the interaction of the reagents; chlorouric acid, salts of alkali metals of ethylenediamine tetraacetic acid, and alkali metal sulfite or ammonium sulfite.

Nakazawa et al., U.S. Pat. No. 4,717,459, which is directed to an electrolytic gold plating solution including a soluble gold salt, a conductivity salt and, in addition, a mixture of a lead compound and a complexing agent.

It is often desirable to operate gold electroplating solutions at pH values lower than neutral; as, for example, in plating on circuitry defined using alkaline-developable photoresists It is characteristic of sulfite gold plating solutions that for stable operation a slight

excess of sulfite ion beyond that required for complexation of the gold should be present in the solution. Additionally, however, the nature of the gold sulfite complex is such that for every ion of gold added to the solution two ions of sulfite are added. When gold is plated out of the solution at alkaline pH the excess sulfite remains, and can become oxidized to sulfate at the anode. Thus the dissolved solids content, and hence the specific gravity of typical sulfite gold plating solutions increases as the solutions are replenished. For certain applications such as high speed plating this characteristic tends to limit the operating lifetime of the solution. Sulfur dioxide begins to be evolved from sulfite-containing solutions at pH values below about 6.5, forming bisulfite ion, which can itself further react to sulfur dioxide and water. If a sulfite gold plating solution could be operated under stable control at pH values below about 6.5, the controlled evolution of sulfur dioxide could be used to remove a portion of the excess sulfite in a manner analogous to that by which excess cyanide is volatilized from acid gold cyanide electroplating systems.

Finally, it is well known in the art that various alloying, brightening and surface-conditioning agents tend to operate best in selective ranges of pH. Extending the operable pH range of sulfite gold plating solutions should thus increase their adaptability for use with such additives.

SUMMARY OF THE INVENTION

In view of the foregoing it is an object of this invention to provide a sulfite gold electroplating solution which is capable of controlled and stable operation at pH values below about 6.5. It is a further object of the invention that deposits from the electroplating solution thus provided should be of acceptable appearance, purity, hardness, ductility and freedom from porosity and other defects. It is yet a further object that the electroplating solution of this invention should be capable of operating in the presence of various alloying and/or brightening agents in such a fashion as to produce alloyed and/or bright gold electrodeposits.

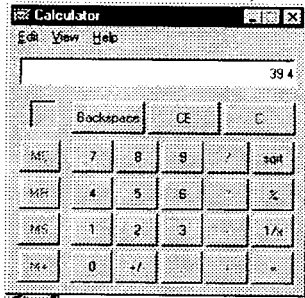
This invention is thus directed to cyanide free gold electroplating solutions and the use thereof, and more particularly to an aqueous solution comprising;

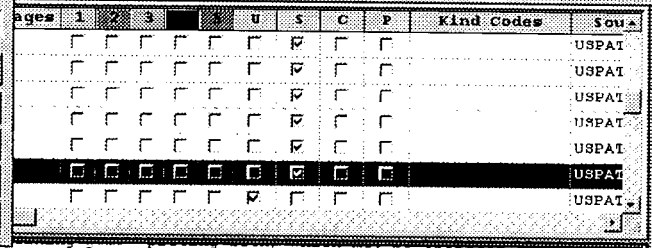
(a) gold in the form of a soluble sulfite complex,
(b) an added source of sulfite and/or bisulfite ion,
(c) a supporting electrolyte;
(d) an organic polyamine or mixture of polyamines of molecular weight from about 60 to 50,000, and
(e) an aromatic organic nitro compound.

In preferred embodiments of this invention, suitable brightening agents and soluble species of suitable alloying metals may be added to the aqueous solution for the purpose of obtaining bright gold or gold alloy electrodeposits.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been discovered that electroplating solutions comprising gold in the form of a soluble sulfite complex, together with an added source of sulfite and/or bisulfite ion and a supporting electrolyte for conductivity and pH control, and also containing both an organic polyamine or mixture of polyamines of molecular weight from about 60 to 50,000 and also an aromatic organic nitro compound, are chemically stable and can be oper-





of 6.1 to 10.5, is disclosed in Camp U.S. Pat. No. 3,397,127, and Shoushanian U.S. Pat. No. 3,475,292 teaches the use of potassium carbonate or potassium tartrate as a buffering and conducting salt in a gold plating bath operated at a pH of 8 to 12 or higher. Haynes et al U.S. Pat. No. 3,475,293 discloses the use of potassium carbonate in a variety of metal baths, Freedman et al. U.S. Pat. No. 3,598,706 teaches the inclusion of tartrates in acid gold plating baths, and Smith U.S. Pat. No. 3,666,640 utilizes tartaric acid as a chelating agent in a gold sulfate formulation.

Brief Summary Text - BSTX (5):

In U.S. Pat. No. 3,893,896, Korbelak et al teach a gold plating solution containing, among other ingredients, an alkali gold cyanide, a weak aliphatic acid, a non-depositing metallic compound, and a metallic hardener. The weak acid may be tartaric, the non-depositing metal may be introduced as a carbonate compound, and the metal hardener may be added as the tartrate; the pH range of the bath is disclosed to be about 3.7 to 4.8. Lerner U.S. Pat. No. 3,926,748 teaches a neutral gold and antimony bath, which includes potassium tartrate and antimony potassium tartrate. The incorporation of alkali metal tartrates in a gold alloy bath that operates at a pH between about 8 and 10 is disclosed in Moriarty et al U.S. Pat. No. 4,121,982.

Brief Summary Text - BSTX (7):

Despite the foregoing, a demand exists for a gold plating bath that is capable of producing electrodeposits of high purity, and particularly one that is capable of producing deposits of sufficient purity to meet the requirements of the semi-conductor industry, using either continuous or pulsed direct current. A need also exists for such a bath of relatively low specific gravity, which is capable of operating under high current density plating conditions at relatively low gold concentrations, and which has a high tolerance to contamination, such as from copper. Finally, there is a demand for a bath having the foregoing features and advantages, from which gold can be alloyed with various metals to produce a variety of characteristics in the deposit, and to extend the range of brightness exhibited thereby.

Brief Summary Text - BSTX (8):

Accordingly, it is a primary object of the present invention to provide a novel plating bath which is capable of producing highly pure gold electrodeposits, and a novel method utilizing the same.

Brief Summary Text - BSTX (9):

It is also an object of the invention to provide such a novel bath and method in which the bath is capable of operating under high current density plating conditions, and is of relatively low gold concentration and specific gravity.

Brief Summary Text - BSTX (11):

It is a further object of the invention to provide such a bath which has a high tolerance to contamination, and which can produce gold alloy deposits of varying karat values and of extended brightness range.

B. Using the baths of part A, coupons are electroplated as described in Example Three A above, with the following results:

Arsenic Modified	
Hardness	Knoop 25 = 96.6
Purity	Gold = 99.95%
	Arsenic = 0.031%

Thallium Modified	
Hardness	Knoop 25 = 123.5
Purity	Gold = 99.56%
	Thallium = 0.43%

C. Adjustments to the pH of the unmodified bath are made with tartaric acid and potassium hydroxide, as appropriate, and plating is carried out in a Hull cell for 2 minutes at 0.5 ampere, to produce the following results:

pH	Bright Range	Efficiency
*6.5	0–15 ASF	115 mg/Amp min.
7.5	0–12.5 ASF	115 mg/Amp min.
8.5	0–15 ASF	113 mg/Amp min.
9.5	0–12.5 ASF	115 mg/Amp min.

*each pH rose to pH 7.5 after test

D. The basic bath is modified with various combinations of copper, cadmium, palladium, zinc and polyethyleneimine to demonstrate the desirability of incorporating those additives; most notable are combinations of copper, cadmium and polyethyleneimine, and of copper and palladium.

EXAMPLE SIX

The uncontaminated bath of Example Three above is tested for use in producing a semi-conductor package in which a silicon chip is bonded by heat and pressure to a gold electroplated surface, and the leads are electrically connected from the gold plated surface to the silicon chip by thermo-sonic or ultrasonic means. In the test, the surface for bonding is first plated with nickel from a sulfamate solution to a thickness of 1.25 micrometers, and is then plated in the gold bath to produce a 1.5 micrometer deposit, using either pulsed or non-pulsed DC current (average current density of 3 ASF). The resultant packages are subjected to standard wire bond test procedures used in the semi-conductor industry, involving evaluation of the assemblies in the "as plated" condition as well as after heat cycling at different temperatures and for varying periods, and satisfy all applicable criteria.

Thus, it can be seen that the present invention provides a novel electroplating bath which is capable of producing highly pure gold deposits, and a novel method utilizing the same. The bath is capable of operating under high current density plating conditions, and is of relatively low gold concentration and specific gravity. It also has a high tolerance to contamination, and is capable of producing gold alloy deposits of varying karat values and of extended brightness range.

Having thus described the invention, what is claimed is:

1. An aqueous gold plating bath comprising, on a per liter basis: about 0.005 to 0.2 gram mole of gold in solution; a tartrate salt providing about 0.1 to 0.4 gram mole of tartrate radical; and a carbonate salt or acid salt providing about 0.2 to 1.5 gram moles of carbonate radical, said bath having a pH of about 7.5 to 13.0.

2. The bath of claim 1 wherein the concentration of gold in solution is about 0.02 to 0.06 gram mole, the concentration of the tartrate salt provides about 0.2 to 0.3 gram mole of the tartrate radical, the concentration of the carbonate salt provides about 0.2 to 0.7 gram mole of the carbonate radical, and said pH value is about 8.0 to 11.0.

3. The bath of claim 1 wherein the concentration of gold in solution is about 0.02 to 0.06 gram mole, the concentration of the tartrate salt provides about 0.2 to 0.3 gram mole of the tartrate radical, the concentration of the carbonate salt provides about 1.0 to 1.5 gram mole of the carbonate radical, and said pH value is about 8.0 to 11.0.

4. The bath of claim 1 additionally comprising a minor amount of a metallic additive selected from the group consisting of thallium, arsenic, copper, cadmium, zinc, palladium, and mixtures thereof.

5. The bath of claim 4 additionally including an additive selected from the group consisting of polyethyleneimine, potassium cyanide, sodium borate, and mixtures thereof.

6. The bath of claim 1 additionally including an additive selected from the group consisting of polyethyleneimine, potassium cyanide, sodium borate, and mixtures thereof.

7. A method for electroplating gold comprising the steps of:

A. immersing a workpiece in a bath comprising, on a per liter basis, about 0.005 to 0.2 gram mole of gold in solution, a tartrate salt providing about 0.1 to 0.4 gram mole of tartrate radical, a carbonate salt providing about 0.2 to 1.5 gram mole of carbonate radical, said bath having a pH value of about 7.5 to 13.0 and a temperature of about 35° to 85° C.; and

B. applying an electrical potential across the workpiece and an anode to provide a current density of about 1.0 to 750 amperes per square foot at said workpiece, to thereby effect the desired thickness of electrodeposited metal thereon.

8. The method of claim 7 wherein said potential is applied by continuous direct current.

9. The method of claim 7 wherein said potential is applied by pulsed direct current.

10. The method of claim 7 including the additional step of adjusting the pH to said value by the introduction of tartaric acid into said bath.

11. As a gold electroplating bath, a solution consisting essentially of about 30 to 60 grams of potassium tartrate, about 30 to 60 grams of potassium carbonate, about 1.5 grams of tartaric acid, about 8 to 12 grams of gold metal, zero to 30 grams of potassium cyanide, zero or an effective amount of an additive selected from the group consisting of thallium, arsenic, copper, cadmium, zinc, palladium, sodium borate, polyethyleneimine, and mixtures thereof, and sufficient water to form one liter of solution.

12. The bath of claim 11 from which potassium cyanide is omitted, and in which the amounts of potassium tartrate and potassium carbonate included are both 60 grams.

13. The bath of claim 11 in which said additive comprises copper, cadmium, and polyethyleneimine, in combination.

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19	US 4717459 A	6												USPAT
20	US 4465564 A	6												USPAT
21	US 4435253 A	4												USPAT
22	US 4396471 A	7												USPAT

electroplating pure, soft, gold metal deposits on a variety of substrates using the specific electrolyte solutions described above wherein the source of the gold metal is an alkali metal or ammonium gold sulphite and two essential additives are thallium and a non-hydroxy, non-amino carboxylic acid.

Brief Summary Text - BSTX (20):

As previously described the essential feature of the present invention is to formulate an alkali metal or ammonium gold sulphite electroplating bath which will consistently produce a pure, bright, soft gold metal deposit on various substrates over a relatively long period of time. The formulation comprises as essential ingredients, an alkali gold metal sulphite, a thallium metal salt, and a non-hydroxy non-amino carboxylic acid. The pH of the bath will range from about 6.0 to 12, and preferably from about 7.5 to 10. Electroplating temperatures will be from about 25.degree. to 80.degree. C. and preferably between about 50.degree. and 65.degree. C.

Brief Summary Text - BSTX (21):

The monovalent gold component is an alkali metal or ammonium gold sulphite. The alkali metal can be sodium, potassium or lithium.

Brief Summary Text - BSTX (22):

The thallium metal component is preferably furnished to the bath in the form of water soluble salts such as the nitrate, sulfate, acetate, halide, carbonate, oxide, hyroxide, sulfite, or oxalate. In the electroplating solutions of the present invention the concentration of the thallium metal in the solution will range from about 0.01 to 0.25 grams per liter, and preferably from about 0.01 to 0.10 grams per liter. In general, the amount of gold metal in the bath will range from about 2 to 25.0 grams per liter.

Detailed Description Text - DETX (3):

A series of runs were conducted to determine the hardness values of gold deposits obtained from a thallium-containing alkali metal gold sulphite electroplating bath solution. The exact procedure employed was to add other additives to the thallium component and then to add the resulting admixtures to the alkali metal gold sulphite electrolyte. The formulations of each run as well as the hardness values are shown in the table set forth below where the amounts of the components are expressed in grams per liter unless otherwise indicated:

Detailed Description Text - DETX (5):

As shown by the above data, the combinations of thallium with oxalic acid and with formic acid produced the desired hardness of less than 90 Knoop. The gold metal deposits in these runs were also bright, and 99.9% plus pure; thereby having ideal characteristics for die bonding and wire attachment as well as tape automated bonding (TAB) applications. In contrast, the use of thallium alone, thallium plus citric acid, and thallium plus EDTA led to unsatisfactory hardness values for electronic uses.

source of the gold metal is an alkali metal or ammonium gold sulphite and two essential additives are thallium and a non-hydroxy, non-amino carboxylic acid.

DETAILED DESCRIPTION OF THE INVENTION

As previously described the essential feature of the present invention is to formulate an alkali metal or ammonium gold sulphite electroplating bath which will consistently produce a pure, bright, soft gold metal deposit on various substrates over a relatively long period of time. The formulation comprises as essential ingredients, an alkali gold metal sulphite, a thallium metal salt, and a non-hydroxy non-amino carboxylic acid. The pH of the bath will range from about 6.0 to 12, and preferably from about 7.5 to 10. Electroplating temperatures will be from about 25° to 80° C. and preferably between about 50° and 65° C.

The monovalent gold component is an alkali metal or ammonium gold sulphite. The alkali metal can be sodium, potassium or lithium.

The thallium metal component is preferably furnished to the bath in the form of water soluble salts such as the nitrate, sulfate, acetate, halide, carbonate, oxide, hyroxide, sulfite, or oxalate. In the electroplating solutions of the present invention the concentration of the thallium metal in the solution will range from about 0.01 to 0.25 grams per liter, and preferably from about 0.01 to 0.10 grams per liter. In general, the amount of gold metal in the bath will range from about 2 to 25.0 grams per liter.

The particular non-hydroxy, non-amino carboxylic acids useful in the present invention are formic and oxalic acids. The amounts of acid employed in formulating the electroplating solutions will range from about 0.20 to 100 and preferably from about 1.0 to 75 grams per liter.

It will be understood that the baths may contain other conventional electroplating additives such as conducting and stability additives. Conducting salts that may be usefully employed include alkali metal or ammonium phosphates, pyrophosphates, sulphate, citrates or borates. On the other hand, stability salts which may be utilized include alkali metal or ammonium sulphites and the like. For most purposes the conducting additive may be used in amounts ranging from about 5 to 100 grams per liter; while the stability additives are used in amounts ranging from about 15 to 50 grams per liter.

Although for most operations the electroplating baths of this invention may be operated at temperatures within the range of 25° to 80° C., and current densities of from about 0.5 to 50 ASF; it will be understood that temperatures, current densities, and treatment times may vary widely depending, of course, upon such factors as the type of substrate employed, the deposit thickness required, etc. The electroplating baths of this invention may be effectively utilized for plating operations both in the electronic field as well as in the decorative field. Illustrative substrates include brass, copper, copper alloys, metallized ceramics, and silicon wafers. As previously discussed, the electroplating baths of this invention are essentially useful in the electronics industry where certain desired grain refinements along with high purity are required in addition to hardness values lower than about 90 Knoop.

It should also be understood that conventional pretreatments, e.g., precleaning, of the substrates prior to being subjected to the plating operations are also contemplated within the scope of the present invention. Thus, for example, a metal substrate such as a brass panel may be subjected to a degreasing step using a hot alkaline solution followed by rinsing with distilled water. The panel may then be dipped in hydrochloric acid or sulfuric acid. Finally, there may be another rinsing treatment with distilled water. Since all of these and other pretreatment or precleaning treatments are well known in the art, the exact procedures employed are not features of the present invention.

The present invention will be more fully understood by reference to the following illustrative embodiments:

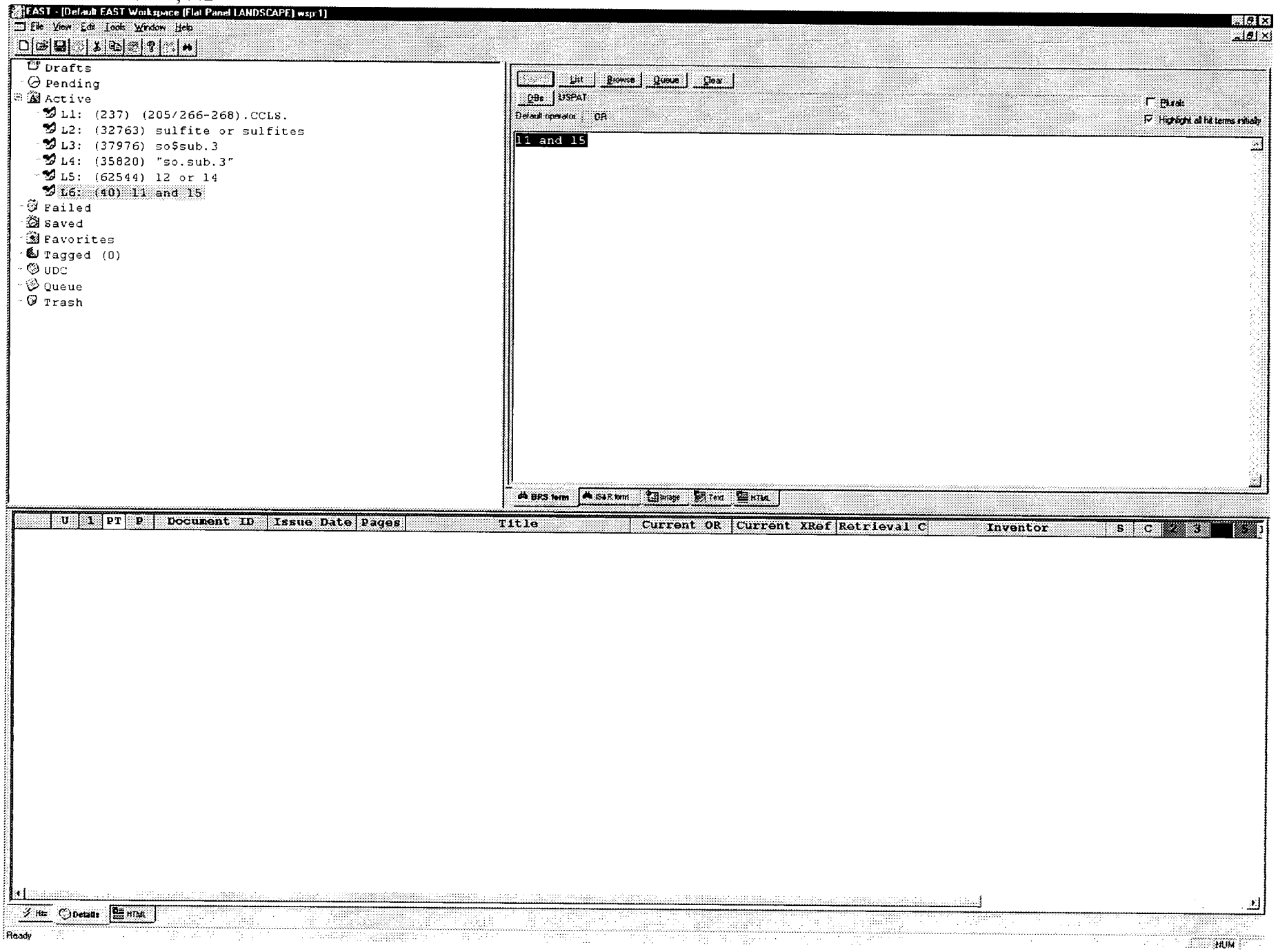
EXAMPLE

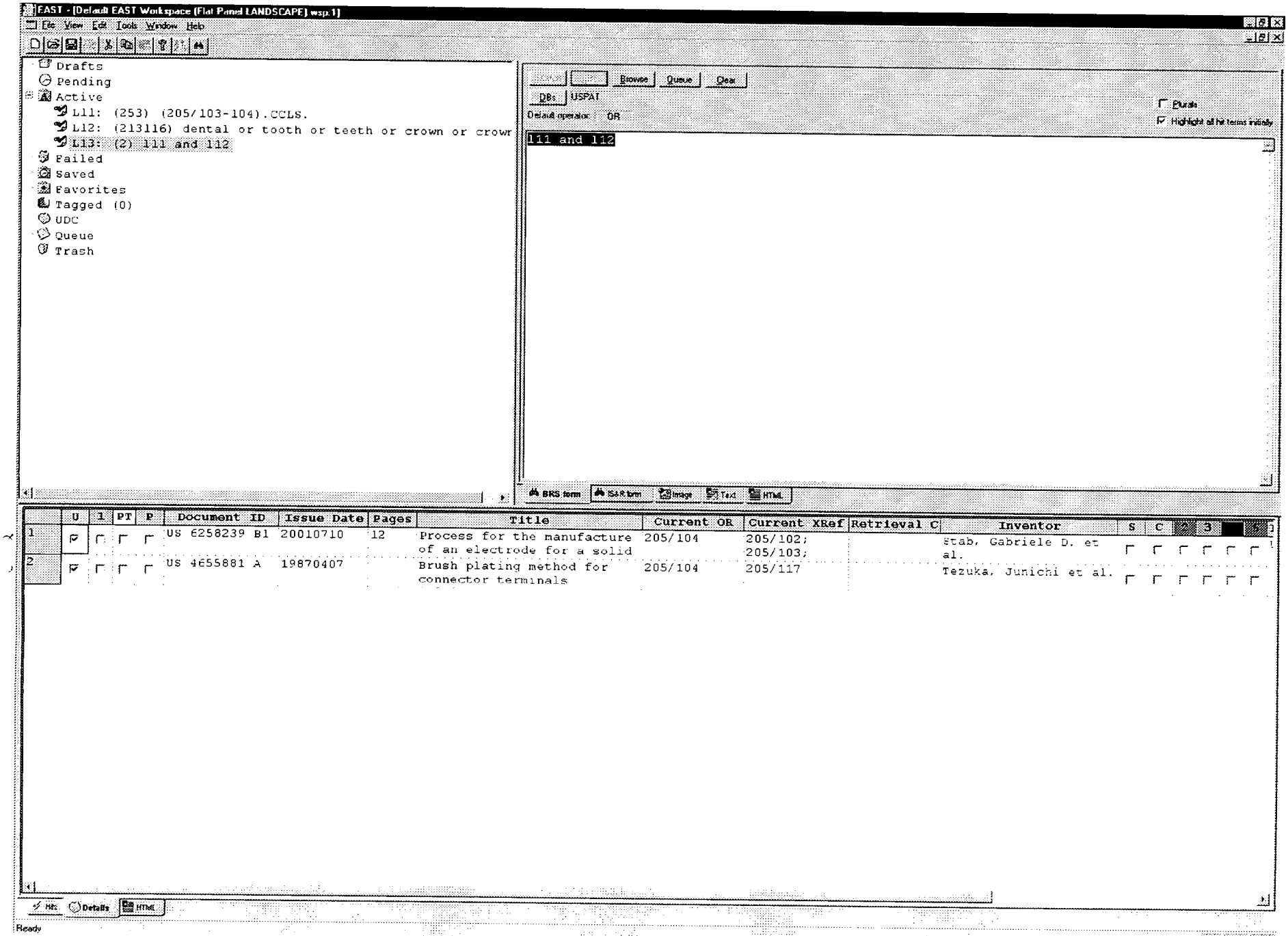
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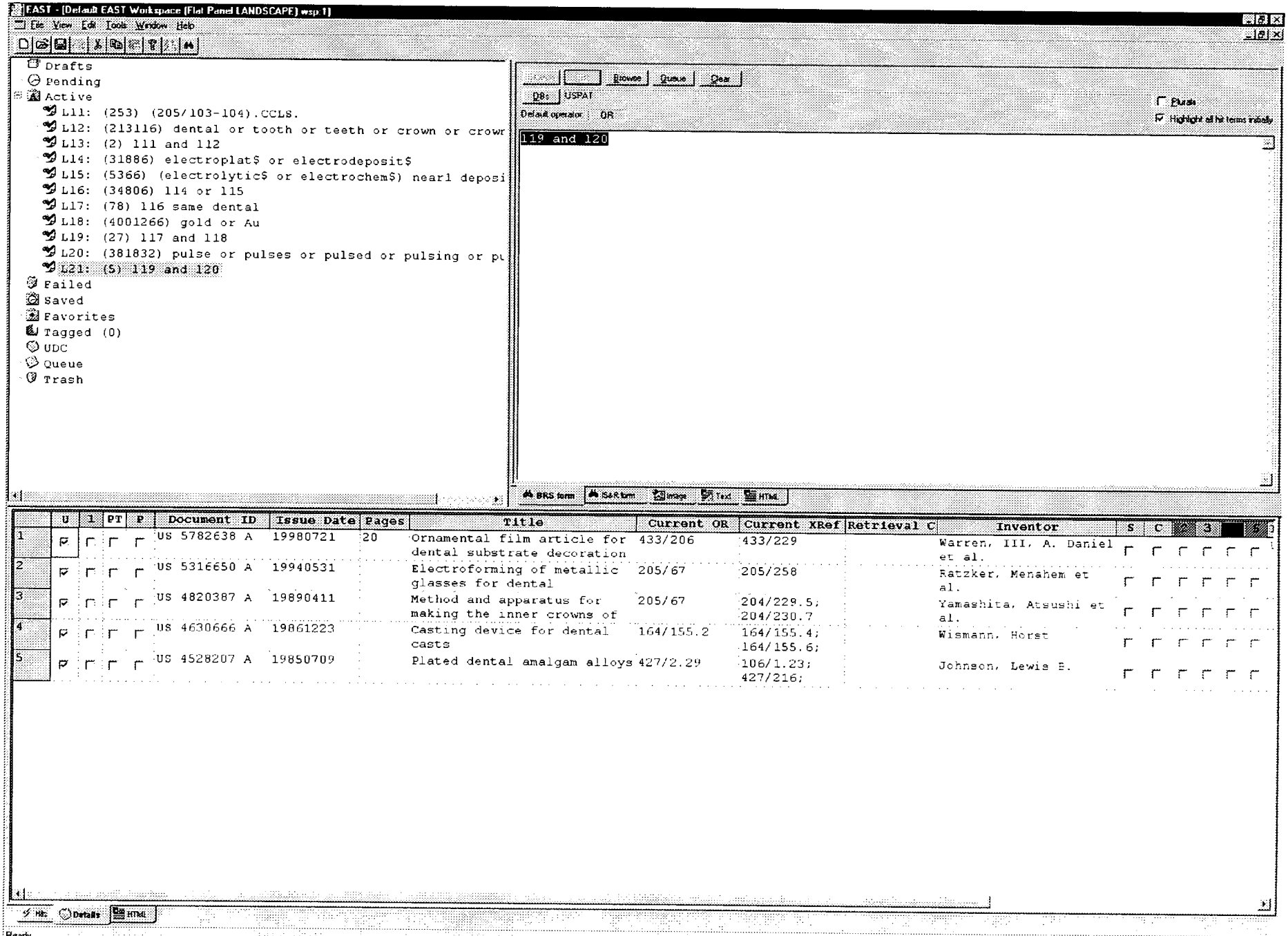
TABLE

	BATH 1	BATH 2	BATH 3	BATH 4	BATH 5	BATH 6
COMPONENTS						
A. Gold as Alkali/metal-sulphite	8	8	8	8	8	8
B. Conducting Salt	50	50	50	50	50	50
C. Stability Salt	30	30	30	30	30	30
D. Thallium, as metal	0.015					
E. Thallium/Citric Acid		0.015/75				
F. Thallium/EDTA			0.015/25			
G. Thallium/Oxalic Acid				0.015/50		
H. Thallium/Formic Acid					0.015/50	
I. Arsenic/Oxalic Acid						0.015/50
INITIAL DEPOSITS						
Electrolysis						
Hardness (Knoop)	135–140	135–140	135–140	60–80	60–80	60–80
Color (Lemon Yellow)	Yes	Yes	Yes	Yes	Yes	Yes
DEPOSITS AFTER 2 AMPS/HR ELECTROLYSIS						
Hardness (Knoop)	135–140	135–140	135–140	60–80	60–80	60–80
Color (Lemon Yellow)	Yes	Yes	Yes	Yes	Yes	Brown

The conducting salt was sodium dibasic phosphate and the stability salt was sodium sulphite. Thallium in the form of thallium sulphate was employed in the runs.


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L4: (35820) "so.sub.3"
L5: (62544) 12 or 14
L6: (40) 11 and 15
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US 6258239 B1
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Process for the manufacture of an electrode for a solid
205/104
205/102; 205/103;
Stab, Gabriele D. et al.
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US 4655881 A
19870407
Brush plating method for connector terminals
205/104
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Tezuka, Junichi et al.
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U | 1 | PT | P | Document ID | Issue Date | Pages | Title | Current OR | Current XRef | Retrieval C | Inventor | S | C | 3
1 | US 5782638 A | 19980721 | 20 | Ornamental film article for dental substrate decoration | 433/206 | 433/229 | Warren, III, A. Daniel et al.
2 | US 5316650 A | 19940531 | Electroforming of metallic glasses for dental | 205/67 | 205/258 | Ratzker, Menahem et al.
3 | US 4820387 A | 19890411 | Method and apparatus for making the inner crowns of | 205/67 | 204/229.5; 204/230.7 | Yamashita, Atsushi et al.
4 | US 4630666 A | 19861223 | Casting device for dental casts | 164/155.2 | 164/155.4; 164/155.6; | Wismann, Horst
5 | US 4528207 A | 19850709 | Plated dental amalgam alloys | 427/2.29 | 106/1.23; 427/216; | Johnson, Lewis E.
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FAST Browser - L21: (5) 19 and 20 | US 4820387 A | Tag: S | Doc: 3/5 (SORTED) | Format: KWIC

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1	US 5782638 A	20										USPAT
2	US 5316650 A	8										USPAT
	US 4820387 A	8										USPAT
4	US 4630666 A	10										USPAT
5	US 4528207 A	4										USPAT

Brief Summary Text - BSTX (20):

According to the present invention, it has now been found that such problems can be solved by applying and solidifying a conductive coating material undissolvable in a plating bath on the working model of the tooth on which the state of a tooth is reproduced, even though it is formed of a non-conductive material such as gypsum or synthetic resin, thereby permitting the thus coated portion to be used as the cathode, and substituting a pulse plating for the D.C. plating which has heretofore been used for making an inner crown composed mainly of thick noble metal deposits layer, thereby passing a pulse current between anode and cathode at a given pulse width and a given pulsed current density and in a given duty cycle [(pulse on-time)/(pulse on-time) +(pulse off-time)]. In addition, the problem that only thin metal deposits are obtained on the concave application face can be solved by fixedly immersing an auxiliary electrode formed of the same metal as the metal to be plated in the plating bath between anode and cathode, while its one end is or is not connected to the anode and its other end if opposite and adjacent to a recess in said cathode.

Brief Summary Text - BSTX (21):

More specifically, the present invention provides a method for making an inner crown of a composite-layered crown for the restoration of crowns, said inner crown being composed mainly of a noble metal, wherein an electrically conductive coating material undissolvable in a plating bath is applied and solidified on an inner crown-forming surface of a working model of a tooth on which the state of the tooth to be restored is reproduced and which is formed of a non-conductive material, and electrical connection is made so as to render said conductive coating material cathodic, while said coating material is immersed in said plating bath; an anode is immersed in said plating bath, while said anode is fixedly located on a position opposite to said inner crown-forming position; an auxiliary electrode formed of the same metal as the metal to be plated is immersed in said plating bath between said anode and said cathode, while its one end is or is not connected to said anode and its other end is opposite and adjacent to a recess in said cathode; and a pulse current is impressed between said anode and said cathode at a pulse width of 0.01 to 50 msec. and a pulsed current density of 1 to 20 A/dm.sup.2 and in a duty cycle of 1 to 30 % for electroplating, thereby making said inner crown. The present invention also provides an apparatus for carrying out the aforesaid method.

Detailed Description Text - DETX (2):

Referring to the drawings, there is shown a working model of a tooth 1 on which the state of the tooth to be restored is reproduced and which is formed of an electrically non-conductive material. As the non-conductive material, use may be made of any suitable material capable of easily reproducing the state of a tooth and being removed from an inner crown electroplated on an inner crown-forming surface position and made primarily of a noble metal without dissolving or damaging it such as, for instance, gypsum that is easily dissolvable by a gypsum dissolver manufactured by GC Dental Industrial Corp. and sold under the trade name of "ROCLEAN" or synthetic acrylic, epoxy and ethyl silicate resins that are burned out upon heated, leaving behind the inner crown. The metal capable of forming an inner crown by electroplating is mainly a noble metal, and should be a noble metal which can be electroplated, and can securely and hygienically be applied under the conditions prevailing in the mouth such as, for instance, platinum, palladium, rhodium, ruthenium, gold and silver that may be used alone or in the form of alloys with iron, nickel, copper, cobalt, molybdenum, tungsten and/or indium. It is understood, however,

United States Patent [19]

Yamashita et al.

[11] **Patent Number: 4,820,387**

[45] **Date of Patent: Apr. 11, 1989**

[54] **METHOD AND APPARATUS FOR MAKING THE INNER CROWNS OF COMPOSITE-LAYERED CROWNS FOR RESTORING CROWNS**

[75] Inventors: **Atsushi Yamashita, Okayama; Ikuo Kyotani, Kitamoto, both of Japan**

[73] Assignee: **G-C Dental Industrial Corp., Tokyo, Japan**

[21] Appl. No.: **168,463**

[22] Filed: **Mar. 15, 1988**

[30] **Foreign Application Priority Data**

Apr. 10, 1987 [JP] Japan 62-85761

[51] Int. Cl.[4] C25D 1/00; C25D 17/00

[52] U.S. Cl. 204/4; 204/231

[58] Field of Search 204/4, 231

[56] **References Cited**

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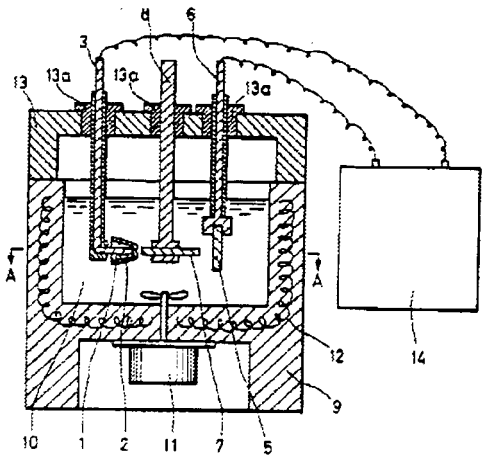
Primary Examiner—T. M. Tufariello

Attorney, Agent, or Firm—Oblon, Fisher, Spivak, McClelland & Maier

[57] **ABSTRACT**

In a method and apparatus for making an inner crown of a composite-layered crown for the restoration of crowns, said inner crown being composed mainly of a noble metal, an electrically conductive coating material undissolvable in a plating bath is applied and solidified on an inner crown-forming surface of a working model of a tooth on which the state of the tooth to be restored is reproduced and which is formed of a non-conductive material, and electrical connection is made so as to render said conductive coating material cathodic, while said coating material is immersed in said plating bath; an anode is immersed in said plating bath, while said anode is fixedly located on a position opposite to said inner crown-forming position; an auxiliary electrode formed of the same metal as the metal to be plated is fixed for immersion in said plating bath between said anode and said cathode, while its one end is or is not connected to said anode and its other end is opposite and adjacent to a recess in said cathode; and a pulse current is impressed between said anode and said cathode at a pulse width of 0.01 to 50 msec. and a pulsed current density of 1 to 20 A/dm^2 and in a duty cycle of 1 to 30% for electroplating, thereby making said inner crown.

14 Claims, 1 Drawing Sheet



EAST Browser - L21: (5) 19 and 20 | US 5316650 A | Tag: S | Doc: 2/5 (SORTED) | Format: KWIC

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	Document ID	Pages	1	2	3		U	S	C	P	Kind Codes	Source
1	US 5782638 A	20										USPAT
	US 5316650 A	8										USPAT
3	US 4820387 A	8										USPAT
4	US 4630666 A	10										USPAT
5	US 4528207 A	4										USPAT

Chung, Kanagawa Shigaku, 22: 32-49, report a metal plate denture electroformed of Ni-CO alloy. In Watanabe et al., Kanagawa Shigaku, 23: 622-628 are reported. Kober et al., Zahnarztl Mitt., 77: 2406-2409. Klett et al. (1987), Dtsch. Zahnarztl Z., 42: 614-617; Klaus, Quintessenz Zahntech, 14: 1229-1240 (1988); Menne, Quintessenz Zahntech, 15: 1057-1064 (1989); and Stroppe, Dental-Labor (Munch), 38: 201-202 (1990), report work concerning electroforming of metals for dental prostheses. However, all of the alloys studied--gold, nickel, or nickel-cobalt--are either not strong enough to be used in thin sections where substantial strength is needed, or they lack biocompatibility.

Brief Summary Text - BSTX (13):

To attain the objects of this invention, there is provided a process of electroforming metals for dental prostheses, wherein metallic glass alloys of cobalt and phosphorus are electrodeposited on a substrate. Although metallic glass alloys have been known for decades, it was neither known nor at all predictable whether a cobalt-phosphorus glass alloy would be satisfactory for dental prostheses in view of the particular mechanical and corrosion-resistance specifications for such prostheses.

Brief Summary Text - BSTX (33):

The electroforming step is conducted at about 40.degree.-85.degree. C., preferably 75.degree. C., and it is also preferred that an inert gas, such as nitrogen, for example, is purged through the bath at a rate of about 1-10 cc/minute. The current may be direct current, preferably applied at between 150-300 mA/cm.sup.2 or, alternatively, a pulsed galvanostatic current, preferably at about 300 mA/cm.sup.2, preferably 200 .mu.s on and 400 .mu.s off. Deposition rate can be improved by ultrasonic agitation, rotation or fast stirring of the solution.

Detailed Description Text - DETX (15):

In order to obtain information on how the Co-P alloys would behave in the mouth, several samples were subjected to accelerated corrosion tests in Hanks' solution (Hanks and Wallace, 1949). The only test performed was a simple potentiodynamic scan of the alloys themselves. These were not electrochemically coupled to other metals likely to be in the mouth such as silver amalgams or gold. No attempts were made to optimize the corrosion behavior by alloying. For these measurements, the surface roughness was not controlled. The samples were studied as deposited and were degreased in a series of solvents prior to immersion in the solution. To obtain a comparison with currently used dental alloys, cast Vitallium.RTM. alloy disks were polished with 4000 grit silicon carbide paper. These were then potentiodynamically scanned at the same rate in the same solution. A fresh solution was used for each experiment The corrosion potential was 200 mV to 300 mV vs. Saturated Calomel Electrode (SCE) for as-deposited Co-P samples and -100 mV to -120 mV vs. SCE for polished Vitallium.RTM. samples. The average corrosion rate (5 samples) was 0.8 mpy for Co-P alloys and 2.3 mpy for the Vitallium.RTM. cast alloy.

Claims Text - CLTX (25):

14. A process according to claim 8, wherein said current is a pulsed galvanostatic current at approximately 300 mA/cm.sup.2 with 200 mu.s on time

US005316650A

United States Patent [19]

Ratzker et al.

[11] **Patent Number: 5,316,650**

[45] **Date of Patent: May 31, 1994**

[54] **ELECTROFORMING OF METALLIC GLASSES FOR DENTAL APPLICATIONS**

[76] Inventors: **Menahem Ratzker**, 1131 University Blvd., West Silver Spring, Md. 20902; **David S. Lashmore**, 5506 Woodlyn Rd., Frederick, Md. 21701; **John A. Teak**, 13446 Pond Filed Ct., Highland, Md. 20777

[21] Appl. No.: **19,489**

[22] Filed: **Feb. 19, 1993**

[51] Int. Cl.[5] C25D 1/10

[52] U.S. Cl. 205/67; 205/258

[58] Field of Search 205/67, 258

[56] **References Cited**

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4,891,183	1/1990	Corwin	420/435
5,088,923	2/1992	Andreiko	433/9

Primary Examiner—T. M. Tufariello

Attorney, Agent, or Firm—Millen, White, Zelano & Branigan

[57] **ABSTRACT**

In a process of electroforming a metal to produce a dental prosthesis, the improvement comprising employing as the metal a metallic glass alloy such as cobalt and phosphorus containing 8-30% by weight of phosphorus. The electrolytic bath comprises:

15-300 g/L $CoSo_4.7H_2O$

40-80 g/L $CoCl_2.6H_2O$

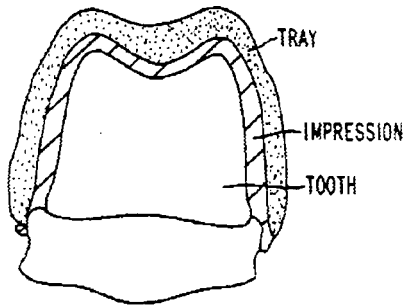
25-35 g/L H_3BC_3

30-100 g/L H_3PO_3

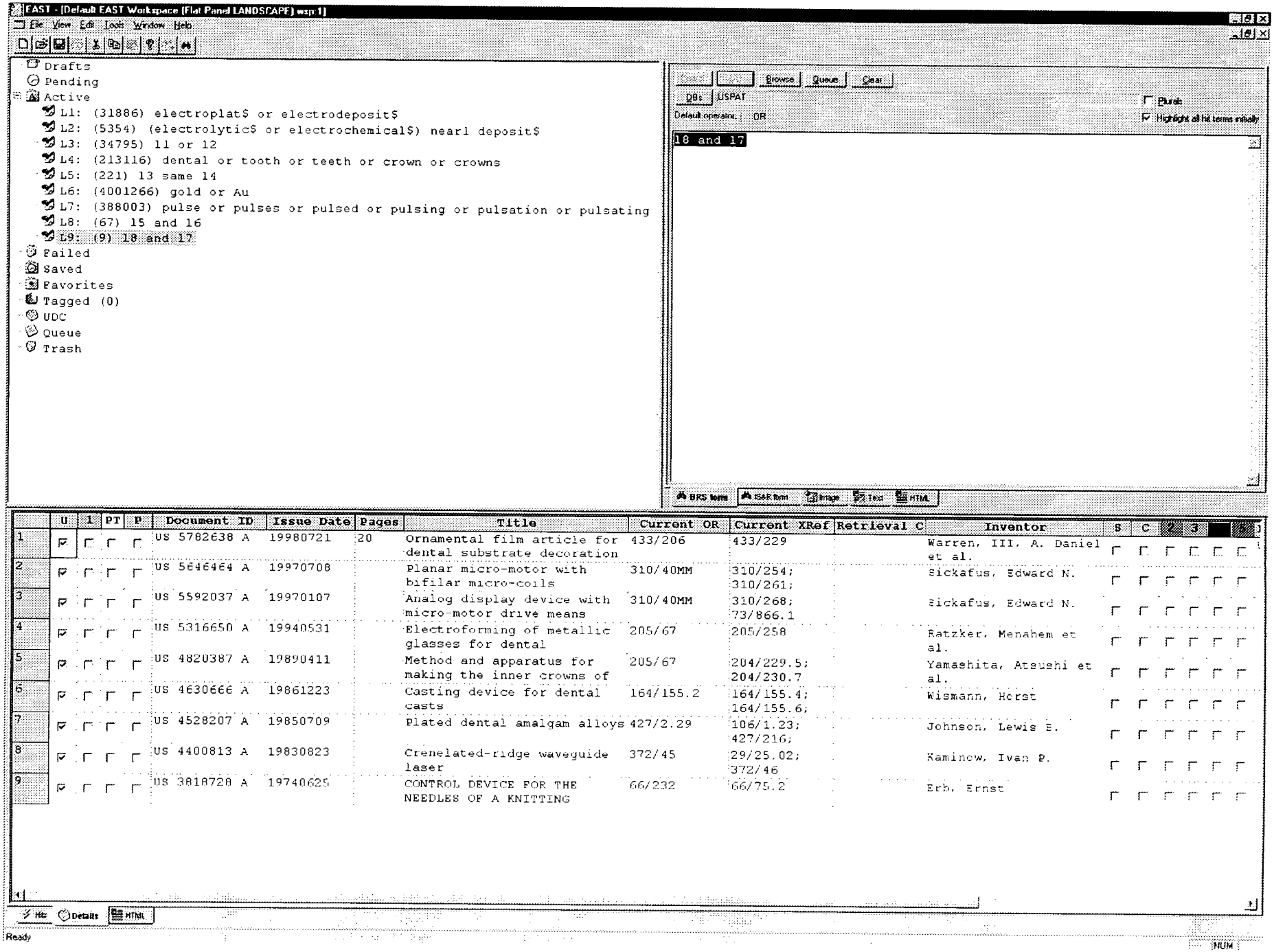
1-2 ml/L wetting agent

pH about 0.8-2.0.

13 Claims, 3 Drawing Sheets



4/2003



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1	☑	☐	☐	☐	US 5782638 A	19980721	20	Ornamental film article for dental substrate decoration	433/206	433/229		Warren, III, A. Daniel et al.	☐	☐	☐	☐
2	☑	☐	☐	☐	US 5646464 A	19970708		Planar micro-motor with bifilar micro-coils	310/40MM	310/254; 310/261;		Sickafus, Edward N.	☐	☐	☐	☐
3	☑	☐	☐	☐	US 5592037 A	19970107		Analog display device with micro-motor drive means	310/40MM	310/268; 73/866.1		Sickafus, Edward N.	☐	☐	☐	☐
4	☑	☐	☐	☐	US 5316650 A	19940531		Electroforming of metallic glasses for dental	205/67	205/258		Ratzker, Menahem et al.	☐	☐	☐	☐
5	☑	☐	☐	☐	US 4820387 A	19890411		Method and apparatus for making the inner crowns of	205/67	204/229.5; 204/230.7		Yamashita, Atsushi et al.	☐	☐	☐	☐
6	☑	☐	☐	☐	US 4630666 A	19861223		Casting device for dental casts	164/155.2	164/155.4; 164/155.6;		Wismann, Horst	☐	☐	☐	☐
7	☑	☐	☐	☐	US 4528207 A	19850709		Plated dental amalgam alloys	427/2.29	106/1.23; 427/216;		Johnson, Lewis E.	☐	☐	☐	☐
8	☑	☐	☐	☐	US 4400813 A	19830823		Crenelated-ridge waveguide laser	372/45	29/25.02; 372/46		Kaminow, Ivan P.	☐	☐	☐	☐
9	☑	☐	☐	☐	US 3818728 A	19740625		CONTROL DEVICE FOR THE NEEDLES OF A KNITTING	66/232	66/75.2		Erb, Ernst	☐	☐	☐	☐

EAST Browser - L10: (12) 9 and 2 | US 4820387 | Tag: S | Doc: 9/12 (SORTED) | "Full" 1/8 (Total images 8)

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4	US 6051117 A	17										USPAT
5	US 5804053 A	13										USPAT
6	US 5603815 A	21										USPAT
7	US 5098544 A	13										USPAT
8	US 4954235 A	17										USPAT
9	US 4820387 A	8										USPAT
10	US 4576685 A	11										USPAT

US-PAT-NO: 4820387

DOCUMENT-IDENTIFIER: US 4820387 A

TITLE: Method and apparatus for making the inner crowns of composite-layered crowns for restoring crowns

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Detailed Description Text - DETX (2):

Referring to the drawings, there is shown a working model of a tooth 1 on which the state of the tooth to be restored is reproduced and which is formed of an electrically non-conductive material. As the non-conductive material, use may be made of any suitable material capable of easily reproducing the state of a tooth and being removed from an inner crown electroplated on an inner crown-forming surface position and made primarily of a noble metal without dissolving or damaging it such as, for instance, gypsum that is easily dissolvable by a gypsum dissolver manufactured by GC Dental Industrial Corp. and sold under the trade name of "ROCLEAN" or synthetic acrylic, epoxy and ethyl silicate resins that are burned out upon heated, leaving behind the inner crown. The metal capable of forming an inner crown by electroplating is mainly a noble metal, and should be a noble metal which can be electroplated, and can securely and hygienically be applied under the conditions prevailing in the mouth such as, for instance, platinum, palladium, rhodium, ruthenium, gold and silver that may be used alone or in the form of alloys with iron, nickel, copper, cobalt, molybdenum, tungsten and/or indium. It is understood, however, that when porcelain is built up and fused on the inner crown for bonding thereunto, or a metal is bonded onto the inner crown by the lost-wax casting process, it is required to use a pure metal or its alloy that is unlikely to be softened and deformed at the fusing temperature of porcelain and the casting temperature of the metal. An electrically conductive coating material 2 is applied and solidified on the inner crown-forming surface of the working model of a tooth 1 so as to use it as the cathode. The conductive coating material 2 should have the property of being not dissolved in a plating bath, and may comprise a combination of a binder, viz., cellulose resin, a mixed cellulose/methacrylate/phenolic resin or a mixed methacrylate/polystyrene resin with about 65 to 70 % of silver powders. A cathodic conducting material 3, which is insulated on its outside, is provided so as to fix and retain the working model of a tooth 1 in place and pass a current through the coating material 2 applied and solidified on the surface of the working model of a tooth 1 to render it cathodic. The cathodic conducting material 3 may extend through the working model of a tooth 1 from its side opposite to the inner crown-forming side, and be exposed at its end on that inner crown-forming side to pass a current through the coating material 2, or may be only embedded and fixed on the side of the working model of a tooth 1 which is opposite to the inner crownforming side. In the latter arrangement, an auxiliary conducting material 4 is needed so as to make electrical connection between end of the coating material 2 opposite to the inner crown-forming side and cathodic conducting material 3. Preferably, the auxiliary conducting material 4 should be insulated on its outer face. When the non-conducting working model of a tooth 1 is formed of gypsum, it is preferred that the working model of a tooth 1 is insulated on the surface area except for the inner crown-forming portion so as to prevent the elution of calcium ions from the gypsum in the plating bath (to be described later), which otherwise results in plating defects. Thus, the provision of such an insulation should preferably be performed

United States Patent [19]

Yamashita et al.

[11] **Patent Number: 4,820,387**

[45] **Date of Patent: Apr. 11, 1989**

[54] **METHOD AND APPARATUS FOR MAKING THE INNER CROWNS OF COMPOSITE-LAYERED CROWNS FOR RESTORING CROWNS**

[75] Inventors: **Atsushi Yamashita, Okayama; Ikuo Kyotani, Kitamoto, both of Japan**

[73] Assignee: **G-C Dental Industrial Corp., Tokyo, Japan**

[21] Appl. No.: **168,463**

[22] Filed: **Mar. 15, 1988**

[30] **Foreign Application Priority Data**

Apr. 10, 1987 [JP] Japan 62-86761

[51] Int. Cl.[4] C25D 1/00; C25D 17/00

[52] U.S. Cl. 204/4; 204/231

[58] Field of Search 204/4, 231

[56] **References Cited**

U.S. PATENT DOCUMENTS

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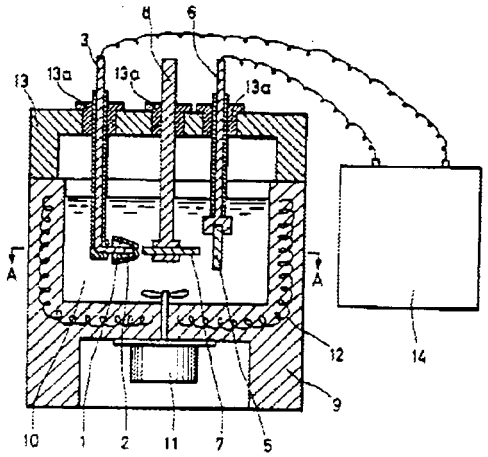
Primary Examiner—T. M. Tufariello

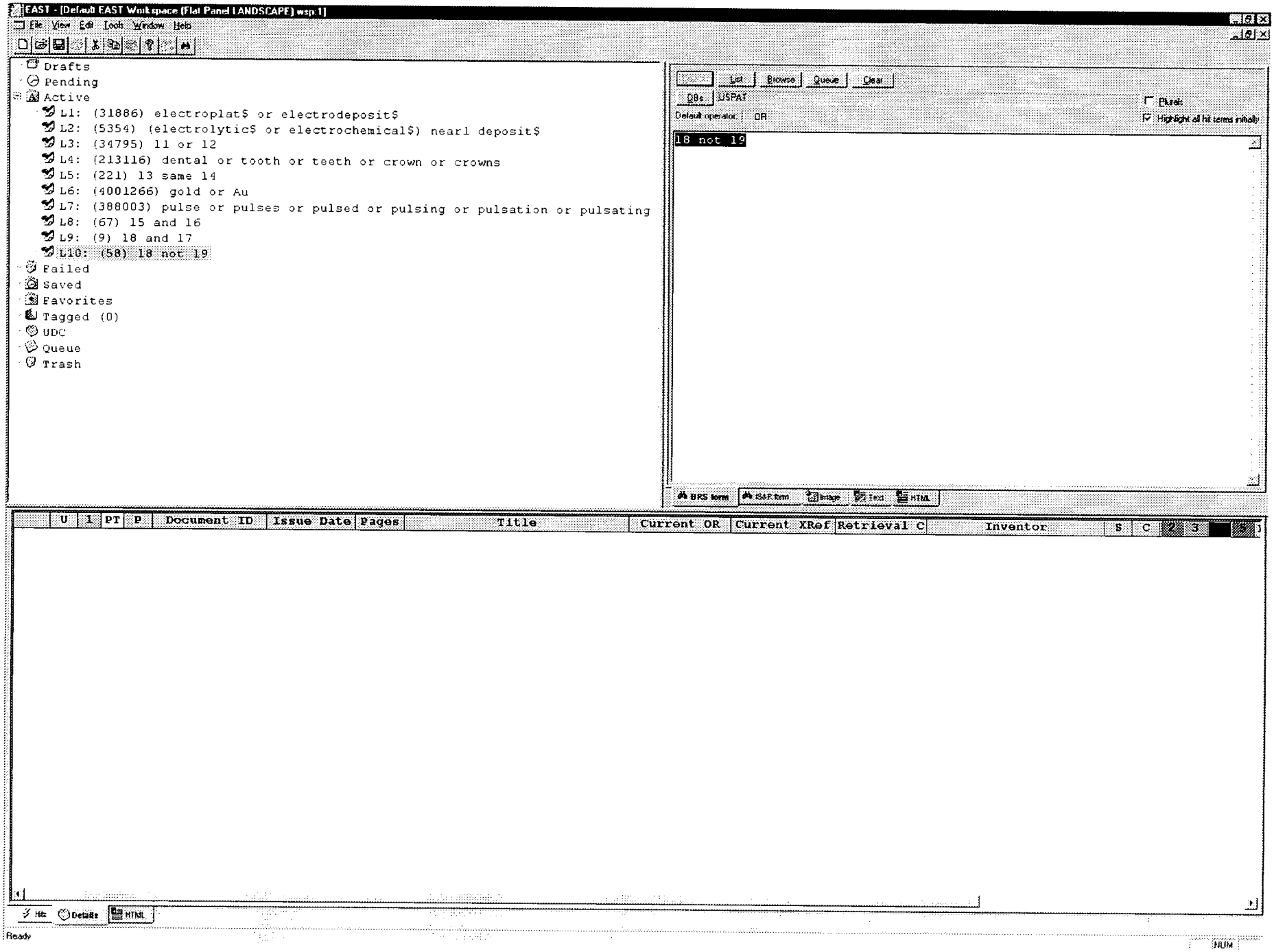
Attorney, Agent, or Firm—Oblon, Fisher, Spivak, McClelland & Maier

[57] **ABSTRACT**

In a method and apparatus for making an inner crown of a composite-layered crown for the restoration of crowns, said inner crown being composed mainly of a noble metal, an electrically conductive coating material undissolvable in a plating bath is applied and solidified on an inner crown-forming surface of a working model of a tooth on which the state of the tooth to be restored is reproduced and which is formed of a non-conductive material, and electrical connection is made so as to render said conductive coating material cathodic, while said coating material is immersed in said plating bath; an anode is immersed in said plating bath, while said anode is fixedly located on a position opposite to said inner crown-forming position; an auxiliary electrode formed of the same metal as the metal to be plated is fixed for immersion in said plating bath between said anode and said cathode, while its one end is or is not connected to said anode and its other end is opposite and adjacent to a recess in said cathode; and a pulse current is impressed between said anode and said cathode at a pulse width of 0.01 to 50 msec. and a pulsed current density of 1 to 20 A/dm^2 and in a duty cycle of 1 to 30% for electroplating, thereby making said inner crown.

14 Claims, 1 Drawing Sheet




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47	US 4392829 A											USPAT
48	US 4295941 A											USPAT
49	US 4288298 A	9										USPAT
50	US 4283839 A	10										USPAT
51	US 4234666 A	10										USPAT

Brief Summary Text - BSTX (3):

The invention has particular though non-exclusive application in the construction of dental implants or dental crowns and, for explanatory purposes only, is herein described in such context. Thus, in the formation of dental implants, the apparatus may be employed for electrolytically etching a substrate and then electroplating a metal coating onto the substrate, which subsequently is to be coated with a dental porcelain. Such a plating process is proposed for the purpose of providing a bond-aiding interface between a high strength alloy substrate and the porcelain. In the context of electroforming, the apparatus may be employed in the formation of a hollow matrix upon which a dental porcelain is subsequently to be deposited for the purpose of producing a dental crown. However, it is to be understood that the apparatus need not be employed solely for electroplating or electroforming objects for use in dentistry, and that the apparatus may be used in the plating or formation of other objects.

Brief Summary Text - BSTX (5):

Electro-deposition techniques, including both electroplating and electroforming techniques, are in general widely understood and documented. However, to the inventor's knowledge, no previous apparatus has been proposed which is suited to the specialised needs which exist in the construction of dental implants and dental crowns. For such purposes, an electro-deposition apparatus should be capable of predictable performance in electro-depositing metal onto either a small number or a large number of substrates, so that the demands of varying work loads may be met. At the same time, the apparatus should not be so operationally complex as to tax the ability of users who are not specialists in the electro deposition field. These are seemingly incompatible requirements which, along with other requirements, the present invention seeks to meet.

Detailed Description Text - DETX (2):

The apparatus as shown in the drawings is suitable for use in electroforming hollow metal articles such as gold matrices for dental crowns. In the absence of a suitable electroforming apparatus, such matrices previously have been hand modelled from platinum. In use of the apparatus, a number of gold matrices are electro-formed to a thickness of approximately 200 .mu.m upon male moulds which are formed from artificial stone. Having electroformed the matrices, they are removed from the apparatus, the artificial stone is removed from the matrices and the matrices are covered with an appropriately configured layer of dental porcelain. The invention is not concerned so much with the production of the complete dental crowns, but with the apparatus for use in electroforming matrices for the crowns.

Detailed Description Text - DETX (4):

For the purpose of electroforming gold, the electrolyte may be constituted by a solution having the following composition:

Detailed Description Text - DETX (5):

United States Patent [19]

Rogers

[11] **4,288,298**

[45] **Sep. 8, 1981**

[54] **METHOD AND APPARATUS FOR ELECTROPLATING OR ELECTROFORMING METAL OBJECTS**

[76] Inventor: **Olbert W. Rogers**, 70 Gymea Bay Rd., Gymea, New South Wales, Australia, 2227

[21] Appl. No.: **129,293**

[22] Filed: **Mar. 11, 1980**

[30] **Foreign Application Priority Data**

Mar. 14, 1979 [AU] Australia PD8025

[51] Int. Cl.³ C25D 1/00; C25D 5/00; C25D 17/06; C25D 17/10

[52] U.S. Cl. 204/4; 204/23; 204/228; 204/297 W

[58] Field of Search 204/3, 4, 14 R, 15, 204/228, 231, DIG. 7, 297 W, 285, 283, 23

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Primary Examiner—T. M. Tufariello
Attorney, Agent, or Firm—Ladas & Parry

[57] **ABSTRACT**

The invention relates primary to the field of dentistry, particularly to the formation of dental crowns, and provides an apparatus for use in electrodeposition of a metal onto a plurality of substrates, which comprises

a retainer for an electrolyte,

a first electrode member having means for supporting said plurality of substrates within said retainer,

a second electrode member having a plurality of support zones for supporting pieces of said metal within said retainer,

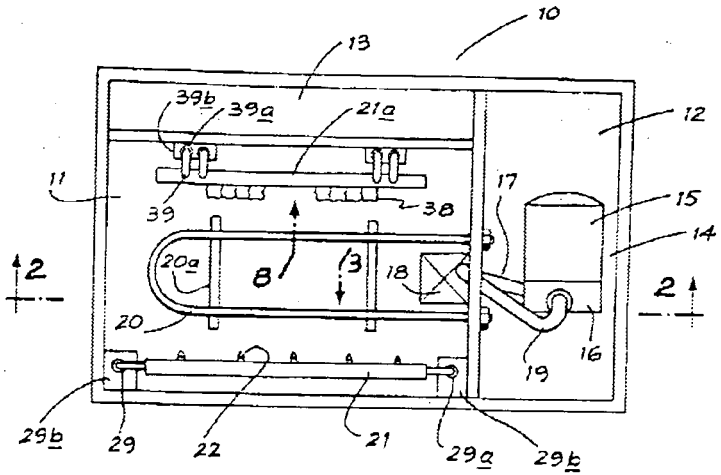
connecting means for mounting the first electrode member in the retainer and intended for connecting the first electrode member to one pole of a direct current supply,

mounting means for mounting the second electrode member in the retainer, and

means for making selective connection of one or more of the electrode support zones to the other pole of the direct current supply.

Generally, each substrate is a tooth replica having a conductive outer coating and mounted on a metal former for screwing into the first electrode member. Also, each support zone is preferable a metal basket for containing a piece of the depositing metal.

5 Claims, 10 Drawing Figures



EAST Browser - L10: (58) 8 not 9 | US 4776795 A | Tag: S | Doc: 37/58 (SORTED) | Format: KWIC

File Edit View Tools Window Help

	Document ID	Pages	1	2	3	4	5	6	7	8	9	Kind Codes	Sou
32	US 5131986 A	13											USPAT
33	US 5104323 A	13											USPAT
34	US 5071363 A	20											USPAT
35	US 4801379 A	8											USPAT
36	US 4780079 A	3											USPAT
37	US 4776795 A	8											USPAT
38	US 4764117 A	7											USPAT

US-PAT-NO: 4776795

DOCUMENT-IDENTIFIER: US 4776795 A

TITLE: Process for making metal artificial tooth parts

---------- KWIC ----------

Brief Summary Text - BSTX (4):

In order to avoid the disadvantages of cast artificial teeth parts, there has already been proposed in DE-OS No. 25 18 355 a process for the production of artificial dental structures wherein an adequate metal is electrolytically deposited on a pre-formed pattern in order to build up the artificial tooth structure on the mold thus formed. Specially for making dental crowns, there is taken an impression of the patient's tooth and a tooth pattern is made according to said impression, said pattern is metallized and introduced in an electrolyte that contains ions of the metal to be deposited so that there is electrolytically deposited on the pattern a metal layer in order to produce a mold to which porcelain is applied, after which the metal mold is finally removed from the porcelain.

Brief Summary Text - BSTX (6):

To avoid said difficulties, there has been disclosed in DE-OS No. 32 18 300 a process for making artificial tooth parts of metal, specially of gold, wherein a pattern of the substitute part is made, a mold is made from the pattern, in the mold a metallic casting of the pattern is produced with a machine specially developed for that, and then this metal cast is galvanically coated in a galvanization center with a mechanically cohesive layer of a noble metal in order, if desired, to provide the substitute part thus obtained, after removal from the mold, with a coating of porcelain, plastic, or the like.

Detailed Description Text - DETX (7):

After applying the intermediate layer 8, the positive pattern with the intermediate layer is immersed in a second galvanic bath in which is present a desired alloy, or is then introduced in several different galvanic baths in order now to deposit galvanically on the intermediate layer 8 one or several layers 10 of high-melting metals, preferably noble metals such as gold . (FIG. 11).

United States Patent [19]

Hornig

[11] **Patent Number: 4,776,795**

[45] **Date of Patent: Oct. 11, 1988**

[54] **PROCESS FOR MAKING METAL ARTIFICIAL TOOTH PARTS**

[76] Inventor: Wolfgang Hornig, Gutenbergstr. 9, 6902 Sandhausen, Fed. Rep. of Germany

[21] Appl. No.: 21,175

[22] Filed: Mar. 3, 1987

[30] Foreign Application Priority Data

Mar. 10, 1986 [DE] Fed. Rep. of Germany 3607915

[51] Int. Cl.[4] A61C 5/10

[52] U.S. Cl. 433/223; 433/200.1; 433/206

[58] Field of Search 433/223, 74, 167, 200.1, 433/206, 208, 213, 214, 215, 218; 264/16, 17, 18, 19

[56] References Cited

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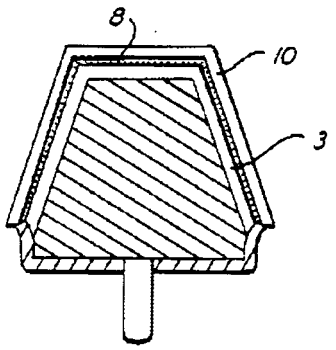
"Metal Sprayed Models from Elastic Impression Materials, A Preliminary Study" from British Dental Journal, Apr. 1965, S.329-332.

Primary Examiner—John J. Wilson
Attorney, Agent, or Firm—Hayes, Davis & Soloway

[57] **ABSTRACT**

The process for making metal artificial tooth parts consists in that an impression of the tooth or jaw to be treated is prepared using an electrically non-conductive material, the inner wall of said impression is coated with a heated low-melting alloy and then the interior is filled up with filling material in which fixing pins are inserted in the case of crowns, inlays and bridges. Alternatively, the impression is filled up with traditional filling materials and an electric conductive coating is produced by vaporizing a metal layer, spraying a conductive lacquer or currentless deposition of an electrically conductive layer. Again, alternatively the impression may be filled up with electrically conductive plastic. The positive pattern so produced is separated from the impression, and there is galvanically applied an intermediate layer of a base metal after which one or more layers of high-melting point metals are galvanically applied to the intermediate layer, the filling material, the innermost electrically conductive layer and the intermediate layer first being then removed and, if desired, porcelain and-/or plastic is applied as facing or substitute teeth on the artificial tooth part thus resulting.

18 Claims, 4 Drawing Sheets



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	Document ID	Pages	1	2	3	4	U	S	C	P	Kind Codes	Sou
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50	US 4283839 A	10										USPAT
51	US 4234666 A	10										USPAT
52	US 4125442 A	8										USPAT
53	US 4064311 A	5										USPAT
54	US 3997637 A	8										USPAT
55	US 3995371 A	10										USPAT

Abstract Text - ABTX (1):

Method of making artificial tooth inlays and crowns by electrolytically depositing a metal, preferably gold, matrix on a preformed model and subsequently building up porcelain on the matrix. The matrix may then be removed prior to cementing the inlay or crown to the patient's tooth ; or alternatively the inlay or crown may be cemented to the patient's tooth together with the matrix.

Inventor Country - INCO (1):

AU

Inventor Group - INGP (1):

Rogers; Olbert William 70 Gymea Bay Road Gymea, New South Wales AU

Priority Country - PRCO (1):

AU

Priority Country - PRCO (2):

AU

Brief Summary Text - BSTX (2):

It is common practice to construct or crown teeth with metal and/or porcelain. Porcelain has the advantage of being aesthetically more acceptable while metal, commonly, but not necessarily gold or gold alloy, is stronger or at least less brittle.

Brief Summary Text - BSTX (3):

One conventional way of constructing an artificial tooth or crown involves forming a model of a patient's tooth, forming a matrix conforming to the shape of such tooth from e.g. platinum foil by burnishing the foil on to the model of such tooth, and thereafter building up and firing porcelain on the foil matrix. Thereafter, the foil is removed from the matrix and the matrix is cemented over the original tooth in the mouth of the patient. Alternatively, a matrix is cast in a metal, e.g. gold alloy, chromium/cobalt or nickel/chromium, and porcelain built up thereon for aesthetic purposes only.

Brief Summary Text - BSTX (6):

According to the present invention a matrix for an artificial tooth construction is formed by electrolytically depositing a suitable metal onto a preformed model and thereafter an artificial tooth construction is built up on the matrix so formed

United States Patent [19]

Rogers

[11] **3,997,637**

[45] **Dec. 14, 1976**

[54] **METHOD OF MAKING TOOTH RECONSTRUCTIONS SUCH AS INLAYS AND CROWNS**

[76] Inventor: **Olbert William Rogers**, 70 Gymea Bay Road, Gymea, New South Wales, Australia

[22] Filed: **Apr. 23, 1975**

[21] Appl. No.: **570,740**

[30] **Foreign Application Priority Data**

Apr. 29, 1974 Australia 7287/74
Dec. 31, 1974 Australia 150/74

[52] **U.S. Cl.** **264/19**; 204/20; 204/30; 264/22; 264/56; 264/129; 264/221

[51] **Int. Cl.²** **A61C 13/8**; A61C 5/10

[58] **Field of Search** 264/16, 17, 22, 19, 264/219, 221, 222, 226, 227, 265, 317, 238, 332, 18, 56, 129; 32/2, 12, 13, 8; 204/20, 30

[56] **References Cited**

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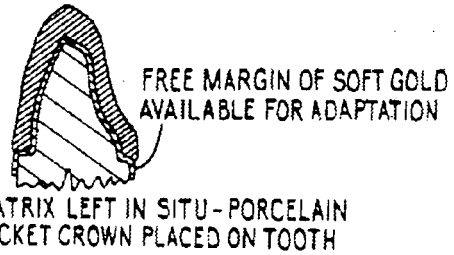
Anon., Technique of Fusing Porcelain to Gold, Julius Aderer, Inc., N.Y., (1939), pp. 2-15 relied on.

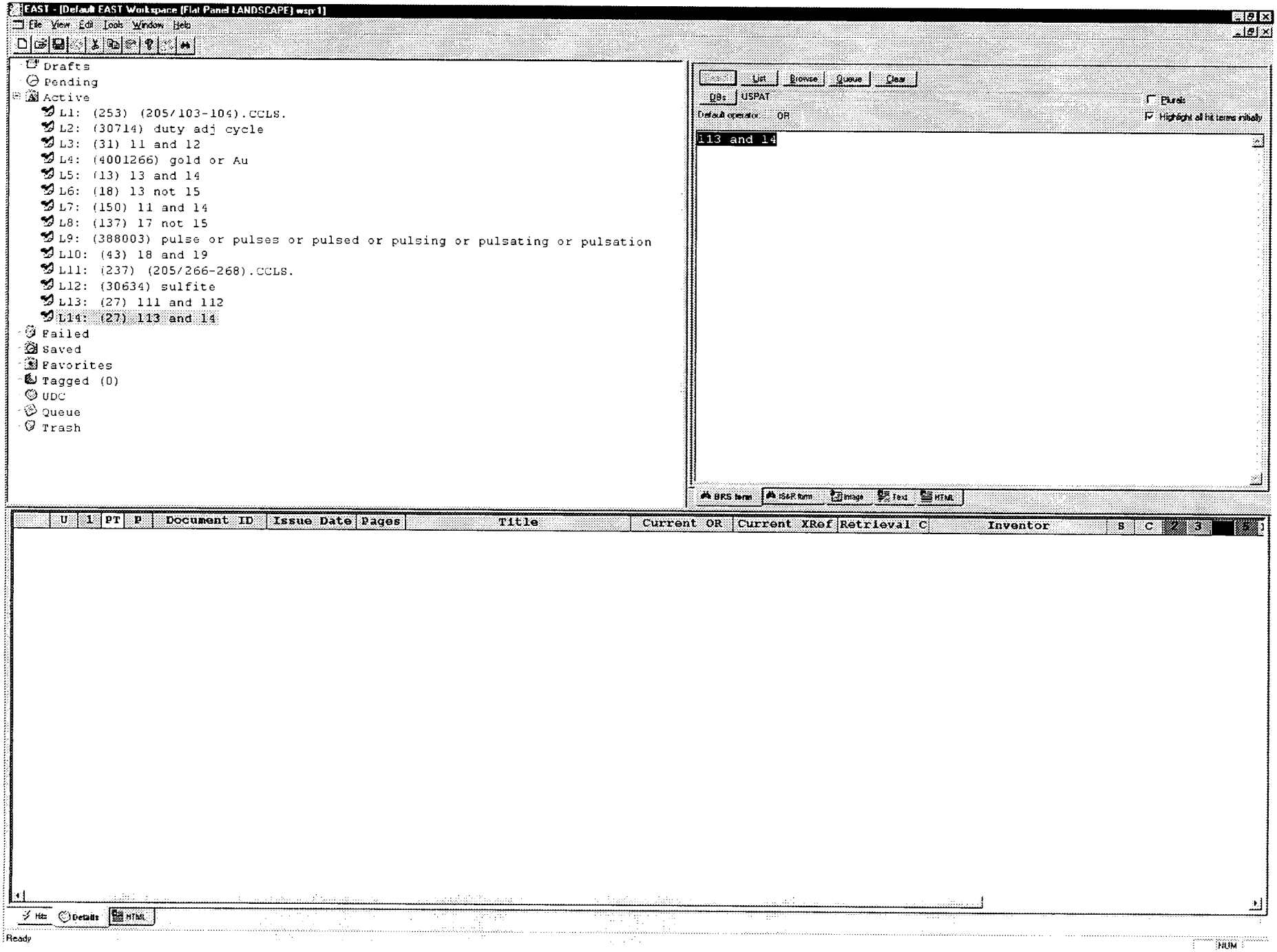
Primary Examiner—Willard E. Hoag
Attorney, Agent, or Firm—Hill, Gross, Simpson, Van Santen, Steadman, Chiara & Simpson

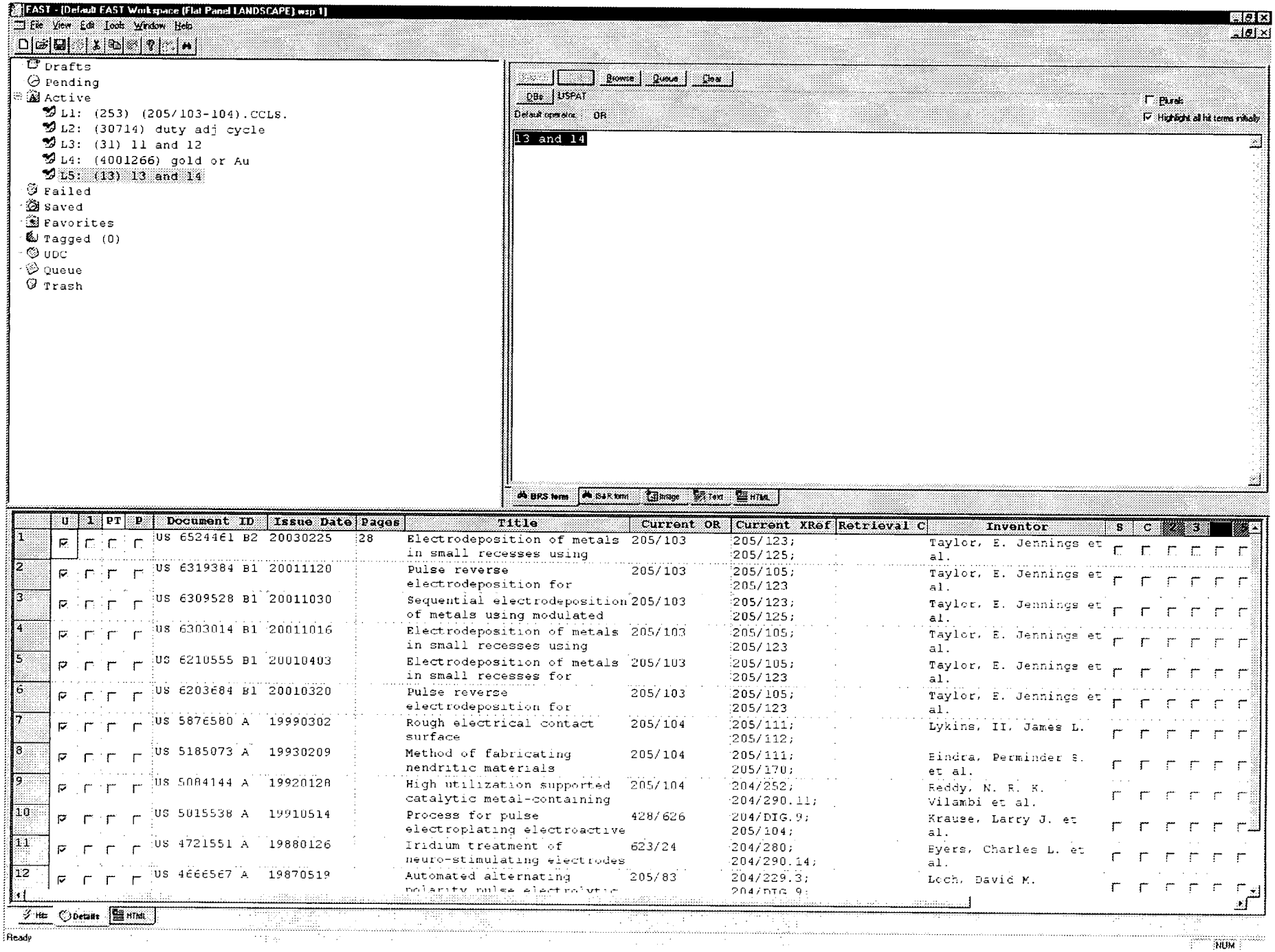
[57] **ABSTRACT**

Method of making artificial tooth inlays and crowns by electrolytically depositing a metal, preferably gold, matrix on a preformed model and subsequently building up porcelain on the matrix. The matrix may then be removed prior to cementing the inlay or crown to the patient's tooth; or alternatively the inlay or crown may be cemented to the patient's tooth together with the matrix.

5 Claims, 43 Drawing Figures




EAST - [Default EAST Workspace (Flat Panel LANDSCAPE) wsp 1]
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Drafts
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L1: (253) (205/103-104).CCLS.
L2: (30714) duty adj cycle
L3: (31) l1 and l2
L4: (4001266) gold or Au
L5: (13) l3 and l4
L6: (18) l3 not l5
L7: (150) l1 and l4
L8: (137) l7 not l5
L9: (388003) pulse or pulses or pulsed or pulsing or pulsating or pulsation
L10: (43) l8 and l9
L11: (237) (205/266-268).CCLS.
L12: (30634) sulfite
L13: (27) l11 and l12
L14: (27) l13 and l4
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1	☑	☐	☐	☐	US 6524461 B2	20030225	28	Electrodeposition of metals in small recesses using	205/103	205/123; 205/125;		Taylor, E. Jennings et al.	☐	☐	☐
2	☑	☐	☐	☐	US 6319384 B1	20011120		Pulse reverse electrodeposition for	205/103	205/105; 205/123		Taylor, E. Jennings et al.	☐	☐	☐
3	☑	☐	☐	☐	US 6309528 B1	20011030		Sequential electrodeposition of metals using modulated	205/103	205/123; 205/125;		Taylor, E. Jennings et al.	☐	☐	☐
4	☑	☐	☐	☐	US 6303014 B1	20011016		Electrodeposition of metals in small recesses using	205/103	205/105; 205/123		Taylor, E. Jennings et al.	☐	☐	☐
5	☑	☐	☐	☐	US 6210555 B1	20010403		Electrodeposition of metals in small recesses for	205/103	205/105; 205/123		Taylor, E. Jennings et al.	☐	☐	☐
6	☑	☐	☐	☐	US 6203684 B1	20010320		Pulse reverse electrodeposition for	205/103	205/105; 205/123		Taylor, E. Jennings et al.	☐	☐	☐
7	☑	☐	☐	☐	US 5876580 A	19990302		Rough electrical contact surface	205/104	205/111; 205/112;		Lykins, II, James L.	☐	☐	☐
8	☑	☐	☐	☐	US 5185073 A	19930209		Method of fabricating nendritic materials	205/104	205/111; 205/170;		Bindra, Perminder S. et al.	☐	☐	☐
9	☑	☐	☐	☐	US 5084144 A	19920128		High utilization supported catalytic metal-containing	205/104	204/252; 204/290.11;		Reddy, N. R. K. Vilambi et al.	☐	☐	☐
10	☑	☐	☐	☐	US 5015538 A	19910514		Process for pulse electroplating electroactive	428/626	204/DIG.9; 205/104;		Krause, Larry J. et al.	☐	☐	☐
11	☑	☐	☐	☐	US 4721551 A	19880126		Iridium treatment of neuro-stimulating electrodes	623/24	204/280; 204/290.14;		Eyers, Charles L. et al.	☐	☐	☐
12	☑	☐	☐	☐	US 4666567 A	19870519		Automated alternating polarity pulse electrolytic	205/83	204/229.3; 204/DIG.9;		Loch, David M.	☐	☐	☐

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EAST Browser - L5: (13) 3 and 4 | US 4666567 A | Tag: S | Doc: 12/13 (SORTED) | Format: KWIC

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7	US 5876580 A	15						☑				USPAT
8	US 5185073 A	15						☑				USPAT
9	US 5084144 A	13						☑				USPAT
10	US 5015538 A	8						☑				USPAT
11	US 4721551 A	16						☑				USPAT
12	US 4666567 A	18						☑				USPAT
13	US 4257853 A	11						☑				USPAT

US-PAT-NO: 4666567

DOCUMENT-IDENTIFIER: US 4666567 A

TITLE: Automated alternating polarity pulse electrolytic processing of electrically conductive substances

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Brief Summary Text - BSTX (5):

Moreover, it is economically advantageous when electroplating precious metals such as gold, silver, rhodium, palladium, etc. to utilize very dilute solutions. This achieves minimum drag out losses and reduces precious metal inventory cost in the solutions. Drag out losses are the plating metal losses which occur as the part being plated is removed from the plating solution. It should be borne in mind, however, that very dilute solutions undergo a reduction in conductivity during plating as the metal ion concentration diminishes. Consequently, the electroplating voltage must increase to maintain a constant current density on the parts being plated. However, as alluded to above, the plating voltage must be maintained below the burn voltage at which the metal deposit becomes unacceptably dull, rough and nodular. Moreover, electroplating at or above the burn voltage results in excessive amounts of molecular hydrogen being infused into the part being plated rendering it imbrittled. In some cases, the part being plated may become etched. However, if the metal concentration in the solution is increased to remedy these effects, it causes the uniformity of the deposit thickness to decrease.

Detailed Description Text - DETX (44):

Also connected to the collector of Q2 through series resistor R11 are back-to-back light emitting diodes LED1 and LED2 which are connected to ground. Light emitting diodes LED1 and LED2 are activated depending on the polarity at terminal X to indicate the same during the duty cycle of the output signal. Terminal Y is connected to the -15 volt terminal on the microprocessor power supply 32.

Current US Cross Reference Classification - CCXR (3):

United States Patent [19]

Loch

[11] Patent Number: 4,666,567

[45] Date of Patent: * May 19, 1987

[54] AUTOMATED ALTERNATING POLARITY PULSE ELECTROLYTIC PROCESSING OF ELECTRICALLY CONDUCTIVE SUBSTANCES

[75] Inventor: David M. Loch, Seattle, Wash.

[73] Assignee: The Boeing Company, Seattle, Wash.

[*] Notice: The portion of the term of this patent subsequent to Oct. 23, 2001 has been disclaimed.

[21] Appl. No.: 663,711

[22] Filed: Oct. 22, 1984

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 289,104, Jul. 31, 1981, Pat. No. 4,478,659.

[51] Int. Cl.[4] C25D 5/18

[52] U.S. Cl. 204/14.1; 204/23; 204/29; 204/228; 204/DIG. 9

[58] Field of Search 204/14.1, 23, 29, 228, 204/DIG. 9

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Primary Examiner—John F. Niebling

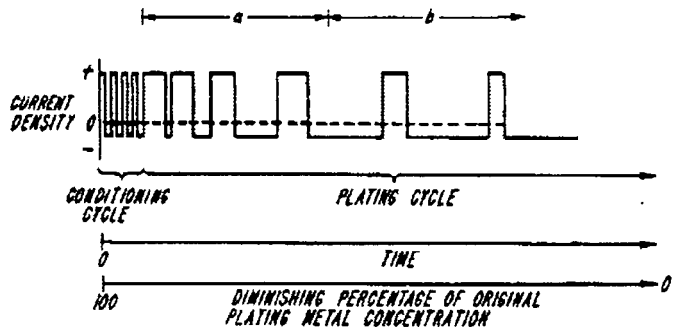
Assistant Examiner—William T. Leader

Attorney, Agent, or Firm—Schwartz, Jeffery, Schwaab, Mack, Blumenthal & Evans

[57] ABSTRACT

A method and apparatus for electroplating the surface of a conductive substrate using an electroplating solution having a low concentration of plating ions. Forward and reverse polarity current pulses are alternatively provided between the part to be plated and an anode in an electroplating bath. The process voltage, V_p, between the part to be plated and the anode is sensed and the time ratio between the forward and reverse current pulses is varied to maintain the process voltage V_p below a burn voltage V_b.

27 Claims, 12 Drawing Figures



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8	US 5185073 A	15							☑					USPAT
9	US 5084144 A	13							☑					USPAT
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11	US 4721551 A	16							☑					USPAT
12	US 4666567 A	18							☑					USPAT
13	US 4257853 A	11							☑					USPAT

US-PAT-NO: 4666567

DOCUMENT-IDENTIFIER: US 4666567 A

TITLE: Automated alternating polarity pulse electrolytic processing of electrically conductive substances

---------- KWIC ---------

Brief Summary Text - BSTX (5):

Moreover, it is economically advantageous when electroplating precious metals such as gold, silver, rhodium, palladium, etc. to utilize very dilute solutions. This achieves minimum drag out losses and reduces precious metal inventory cost in the solutions. Drag out losses are the plating metal losses which occur as the part being plated is removed from the plating solution. It should be borne in mind, however, that very dilute solutions undergo a reduction in conductivity during plating as the metal ion concentration diminishes. Consequently, the electroplating voltage must increase to maintain a constant current density on the parts being plated. However, as alluded to above, the plating voltage must be maintained below the burn voltage at which the metal deposit becomes unacceptably dull, rough and nodular. Moreover, electroplating at or above the burn voltage results in excessive amounts of molecular hydrogen being infused into the part being plated rendering it imbrittled. In some cases, the part being plated may become etched. However, if the metal concentration in the solution is increased to remedy these effects, it causes the uniformity of the deposit thickness to decrease.

Detailed Description Text - DETX (44):

Also connected to the collector of Q2 through series resistor R11 are back-to-back light emitting diodes LED1 and LED2 which are connected to ground. Light emitting diodes LED1 and LED2 are activated depending on the polarity at terminal X to indicate the same during the duty cycle of the output signal. Terminal Y is connected to the -15 volt terminal on the microprocessor power supply 32.

Current US Cross Reference Classification - CCXR (3):

excessive reverse pulse durations would produce dissolution of the material plated on the part and a dull coating appearance. A simultaneous reduction in the forward pulse duration after a small increase in reverse pulse duration will permit a continuing decrease in the forward/reverse pulse duration ratio without having reverse pulses of an excessive length.

PROCESS DESCRIPTION

A comparison of a prior art anodizing current waveform with the waveform of the present invention is illustrated in FIGS. 2A and 2B. FIG. 2A shows a variable polarity waveform as disclosed in U.S. Pat. No. 3,983,014. While not directly analogous to the plating process of the present invention, the anodizing currents disclosed in U.S. Pat. No. 3,983,014 may assist in obtaining a better understanding of the present invention. According to the prior art, a forward pulse of a fixed duration is followed by a slightly shorter reverse pulse of a fixed duration in a periodic manner until either the desired coating thickness is reached or the coating breakdown voltage is reached. It should be understood that the duration of one complete cycle in the FIG. 2A waveform is typically one-tenth of one second or less as opposed to waveform durations of one microsecond or more in the FIG. 2B embodiment for the plating cycle. It should also be noted that FIG. 2B does not show zero current periods between positive and negative current pulses, although such finite periods actually exist. The zero current periods are omitted in the figure to denote a relatively short off-time between pulses compared to the pulse durations themselves.

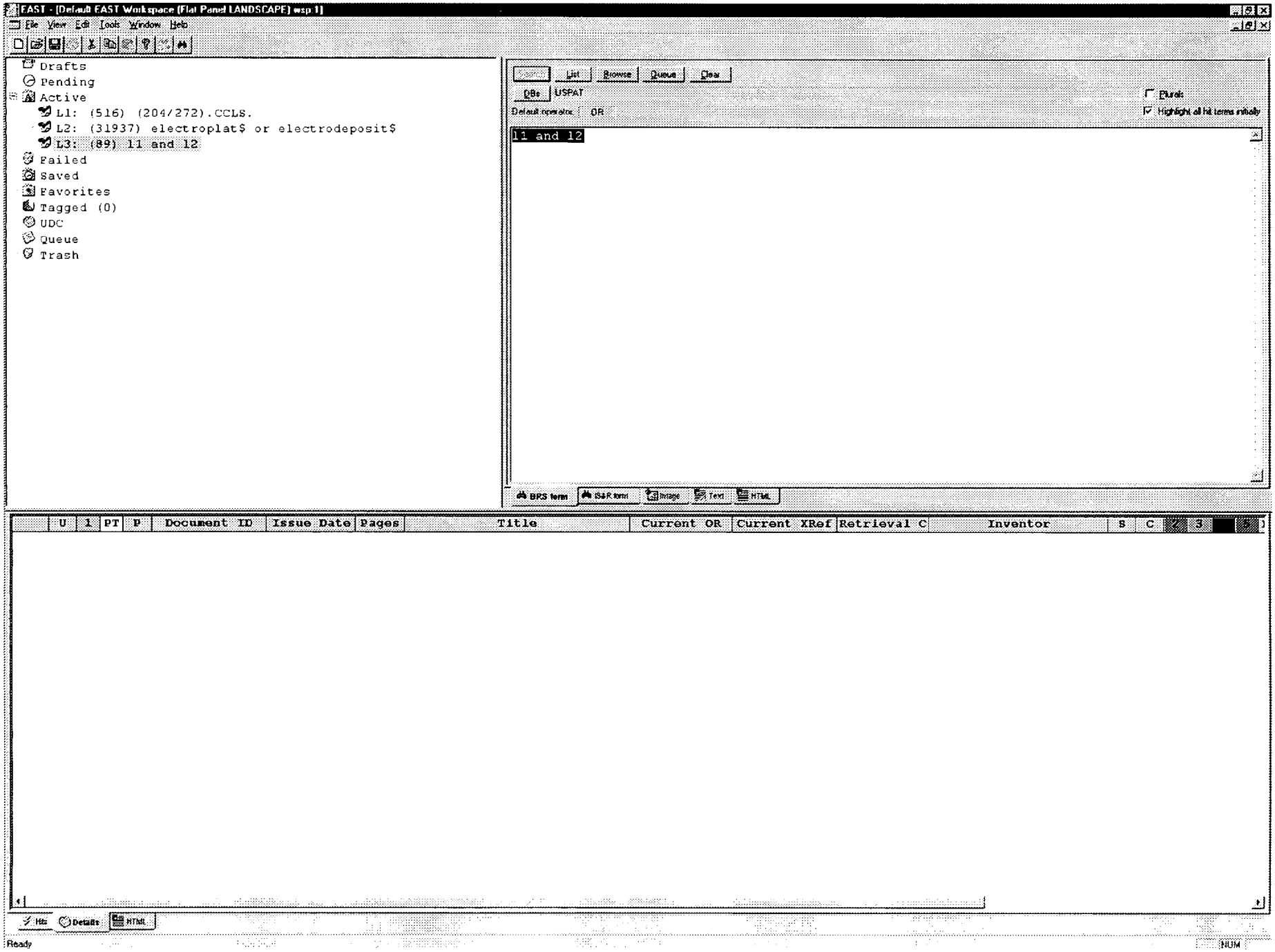
The present invention is characterized by two separate cycles—the conditioning cycle and a plating cycle. The conditioning cycle, which may last 10 minutes, comprises short and constant duration pulses of both forward and reverse current polarity which "condition" the substrate in order to improve the deposit adhesion to it. The plating cycle shown in FIG. 2B is divided into two phases, phases a and b. Each of these phases includes a reduction in the time ratio of forward to reverse power applied. During phase a, a decreasing duration forward pulse is interrupted by an increasing duration negative pulse. In phase b, if further plating is necessary in order to build up an extremely thick coating or the solution is to be exhausted of plating ions, the pulse durations of forward and reverse pulses are maintained constant and the amplitude of the forward current pulses is decreased. In many instances, phase b is unnecessary because a sufficiently thick coating can be built up during phase a. However, it should be understood that phase b can advantageously be included with phase a when necessary. Furthermore, as long as the time ratio of forward to reverse power is decreasing as a function of plating ion depletion, the precise phase utilized is not of crucial importance. As should now be clear to the artisan, the magnitude of the reverse current flow could be increased while the forward current flow is constant or decreased in order to decrease the forward to reverse power ratio. Furthermore, combinations of phases a or b can be altered to provide a greater or quicker decrease in the forward to reverse power ratio.

In the embodiment of FIG. 2B, at the beginning of phase a, a maximum forward pulse may be applied for about 30 milliseconds followed by a reverse pulse applied for about 0.5 milliseconds. As the concentration of plating metal ions decreases, the process voltage increases to maintain a constant current input. In order to control the process voltage, the forward and reverse pulse duration ratios change in accordance with, for example, microprocessor instructions or the like, which are dependent upon the instantaneous process voltage V(t) necessary to maintain the appropriate current level. Toward the end of the plating cycle, when the coating has attained its maximum thickness, the final current waveform is such that the forward pulse duration is at a minimum value and the reverse pulse duration is at a maximum value. For example at the end of phase a, the forward pulse duration may be on the order of 5 milliseconds seconds and the reverse pulse duration on the order of 20 milliseconds. The maximum forward pulse duration and maximum reverse pulse duration illustrated are not drawn to scale and reflect only relative changes in pulse durations of forward and reverse pulses.

As noted earlier, in many instances, the maximum coating thickness is not desired, and in the preferred embodiment, the complete waveform alteration pattern shown in FIG. 2B is not required nor is maximum depositing ion concentration depletion required, and in the preferred embodiment, the complete waveform alteration pattern shown in FIG. 2B is not required in order to control the process voltage. The process voltage to the microprocessor control is illustrated in FIG. 1B where V_p is the process voltage applied between the part and the anode at any point in time. It should be understood that the excursion or variation of V_p shown in FIG. 1B is purely illustrative and intended only to depict the general automated voltage trend of a preferred embodiment. Voltage limits V_1 and V_2 are independently adjustable to control the process voltage excursions, thereby controlling the coating thickness and properties as well as the degree of plating ion concentration in the electroplating solution. V_1 is defined as the process voltage at which the microprocessor begins to alter the initially applied waveform by decreasing the forward to reverse power ratio. V_2 is the process voltage at which the microprocessor would generate a final waveform configuration which would have a forward pulse minimum duration and a reverse pulse maximum duration. A reduction of plating current density could be utilized if the process voltage tended to go above V_2 by means of a suitable voltage limiting constant current controlled forward power supply.

A functional block diagram of one embodiment of the present invention is shown in FIG. 3 which includes the standard plating tank containing an ambient temperature or heated electroplating solution 12. The solution 12 may be air or mechanically agitated. A solution inert anode or an anode of the metal being deposited 14 is provided in the tank to complete the current flow path to the part 16 which is to be plated. Where soluble anodes are used during operation of the apparatus, particles may flake off the anode. Therefore, a loose bag 17 of material unaffected by the electroplating solution, such as "Dynel" can be arranged around the anode to retain any particles. The anode 14 and the part to be plated 16 are connected to a power driver 18 which is supplied by positive (plating) and negative (diffusion) power supplies 20 and 22 respectively. An analog to digital converter 24 samples the voltage applied between the anode and the part to be plated and provides an input to the waveform generator and controller 26. The controller may include a visual display 28 and

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	US 1759171 A	3										USOCR
201	US 1746751 A	4										USOCR
202	US 1723659 A	3										USOCR
203	US 1712244 A	5										USOCR
204	US 1688060 A	3										USOCR
205	US 1524927 A	4										USOCR
206	US 1475198 A	7										USOCR

US-PAT-NO: 1759171

DOCUMENT-IDENTIFIER: US 1759171 A

TITLE: Means for electroplating tubes internally and externally

DATE-ISSUED: May 20, 1930

INVENTOR: SODERBERG VICTOR L; ROY GLEASON C

US-CL-CURRENT: 204/242, 204/297.07 , 204/297.13 , 205/151

May 20, 1930. V. L. SODERBERG ET AL 1,759,171 MEANS FOR ELECTROPLATING TUBES INTERNALLY AND EXTERNALLY Filed May 12, 1927 -9

Patented May 20, 1930 1 9 7 5 9 9 1 7 1 UNI,TED S..RATES PATENT OFFICE VICTOR L. SODERBERG, OF DETROIT, XICHIGAN, AND C. ROY GLEABON, OF CHICAGO, ILLINOIS XR"S FOR ELECTROPLATING TUBES INTERNALLY AND)EXTERNALLY Application filed M;ay i2,1927. Serial No. 290,771. tubular niember both internally and extei-nauy. Sc far as we a,-e owai-e it lia.,; li(@,i-etofore be@n the practice first to plate citlier the inlier or the outer side aiid then the otlici- iri -c order tc secui iiiliferiii distribtitioii of tlit, electro-deposited iiietal. The object of the I)reseiit inveiitioil is to make it feasible siiilultaneolisly to plate botli 20 the iiiside and the outside of the tube or niember having parts that are iiioi-c or less tiil)iiler, iii a siniple iiianner; e.,il)ccizilly iii the cise of 'cliromium @lating@ The various feature@s bf ncvelty %N,Iiei-el)y 15 our inventioii i@ cha@racterized w'ill liereiiiiafter be poiiited otit with particularity iii the claiins; but, for a ftill uiiderstandiiig of our invention and of its objects and a(ivttii@ages. refei-ence may be liad to the folloin,- 20 ing detailed descriptioii taken ir, co'iinectioil with the acconil)anyiii(r di@swiiig, wherein: Figure 1 is a view @'artly in elevation and partly iii section of a tube tc be ele et roplated inte,i-iially and externally an(i lioldiiicr iricaiis 25 tlierefor, the electrol)lating appilti-ati7s being ijidicated more or less di agraiiimatically; an(I Fig. 2 is e section takeii -oii Iiiie 2-2 of Fi(r. 1. Iii the drawiiigs we liave illustrated our i iveittioii as applied to the el I ee troplatiii(, 30 iiitei-iially iind ext-pi-iially of a siinl)le ttil)(@ and the detailed description wall I)c confiiie(i to this exainple; as it will be uiiderstood tI.i-.tt oilly the deta-ils of the coiiibined anode liolder need be chaii,(,ed tc adept it to I)Iatiiig 35 exteriiary or inte'rnally, (rlel)c Valves, T's, p"et cocks @nd pltinibing fixtiti-es and labcratory fixtures in (reneral. Re:ferrin@g to the drawing, A represents the 40 tube to be elect,roplated witli chromium or other metal. This tube is first placed -iii a suitable holder whicli constittites oiie of the aiiode's. In the arrangement shown, the holder consists. of a rod 1 of metal, preferably iron. . Arranged on this rod itte-@- clafiiping 45 heads in the form of cups haviiig their open sides diitected tow'ard each other. Each 'ctip conieniently- co@sists of a-.,nietal sleeve 2 cl'osed at one end with-a block 3 of insulating material not'affwted by the electi-olyte to be 50 enipl@yed ski i'n@g into a counterboi-c iii the lt is sollictiiics ii(@(!(!ssiiry to cle(:trol)late a @ sleeve; t.he rc(I beiiiig coaxitt Witli tlle aii(I passiiig tlirotig li the I)ottoins of tile lattel-. Eacli cf tli(,@ sleeve insiiihers liis ciie or ititil(l, in(t pi-eferal)ly a pluritlity cf lioles 4 exteri(l' t'. ' th 11(digli the wall tliereof and is cctiiit(,,rsunk 55 , 'it the ciid forming the niouth of the CU1), as indicated at 5, to I)rovi(le a seat to receive ofic ell(I cf tlle w6rk aii(I tlitts

May 20, 1930. V. L. SODERBERG ET AL 1,759,171

MEANS FOR ELECTROPLATING TUBES INTERNALLY AND EXTERNALLY

Filed May 12, 1927

Fig. 1.

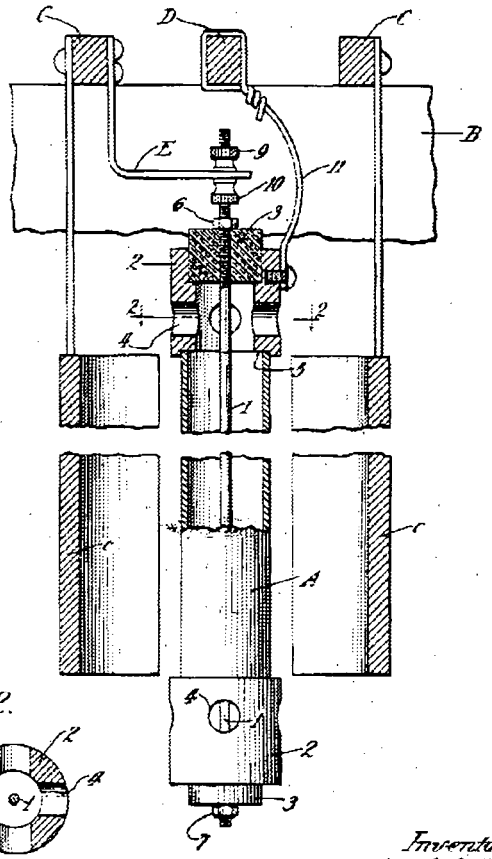


Fig. 2.

Inventors:
Victor L. Soderberg,
By C. Roy Gleason,
Wm. G. Brandenwick,
Atty.

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	US 0902892 A	4	☐	☐	☐	☐	☐	☐	☑	☐	☐		USOCR
218	US 0899827 A	3	☐	☐	☐	☐	☐	☐	☑	☐	☐		USOCR
219	US 0897291 A	3	☐	☐	☐	☐	☐	☐	☑	☐	☐		USOCR
220	US 0891361 A	8	☐	☐	☐	☐	☐	☐	☑	☐	☐		USOCR
221	US 0884075 A	2	☐	☐	☐	☐	☐	☐	☑	☐	☐		USOCR
222	US 0883756 A	5	☐	☐	☐	☐	☐	☐	☑	☐	☐		USOCR
223	US 0881010 A	5	☐	☐	☐	☐	☐	☐	☑	☐	☐		USOCR

US-PAT-NO: 0902892

DOCUMENT-IDENTIFIER: US 0902892 A

TITLE: OCR SCANNED DOCUMENT

DATE-ISSUED: November 3, 1908

INVENTOR: Name not available

US-CL-CURRENT: 205/151, 204/229.4 , 204/272

NOOCRTEXT

BEST AVAILABLE COPY

G. A. LUTZ.

METHOD OF AND APPARATUS FOR ELECTROPLATING.

APPLICATION FILED JUNE 27, 1908.

902,892. Patented Nov. 3, 1908.

Fig. 1.

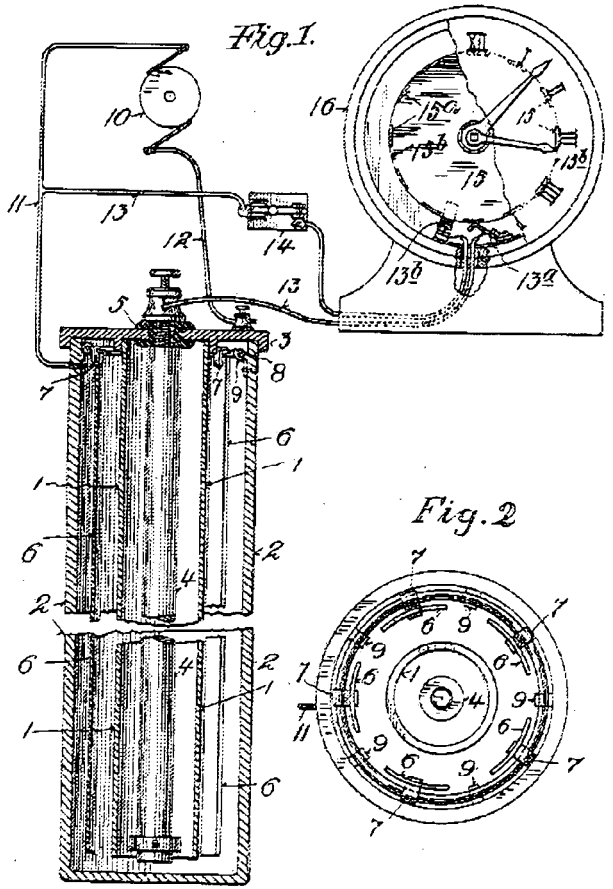


Fig. 2

Witnesses:

Inventor
Geo A. Lutz.
By his Attorney
F. Bourne

FAST Browser - L3: (89) 1 and 2 | US 6168691 B1 | Tag: S | Doc: 13/89 (SORTED) | Format: KWIC

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	Document ID	Pages	1	2	3	4	5	U	S	C	P	Kind Codes	Sou
8	US 6261433 B1	23							☑				USPAT
9	US 6254759 B1	13							☑				USPAT
10	US 6228242 B1	6							☑				USPAT
11	US 6224721 B1	9							☑				USPAT
12	US 6217725 B1	41							☑				USPAT
*	US 6168691 B1	13							☑				USPAT
14	US 6153065 A	10											USPAT

US-PAT-NO: 6168691

DOCUMENT-IDENTIFIER: US 6168691 B1

TITLE: Device for electrochemical treatment of elongate articles

---------- KWIC ----------

Brief Summary Text - BSTX (7):

After treatment in the active baths, the workpieces and mountings must be rinsed very carefully especially when, because of the masks used for screening the areas on the workpiece which have not to be coated, high carry-over has to be taken into account. In order to avoid this problem, an electroplating mounting is proposed in the publication DE 25 24 315 A1 for receiving a plurality of bar-shaped preferably cylindrical objects, such for example as piston rods. The cylindrical rods contained in collar-shaped receiving parts should be coated at the periphery with as uniform a layer thickness as possible. Since the anodes lying opposite the bars on both sides cause an elliptical distribution of layer thickness, however, it is suggested that the bars be turned around their longitudinal axis during the electrochemical treatment. By means of protective shells, which are longitudinally adjustable and individually coordinated to the item to be treated, the metal layer is delimited at their ends in the longitudinal direction of the bars. The plating mounting is designed in such a way that it can be accommodated to the length of the bar by means of vertically adjustable side parts.

Brief Summary Text - BSTX (8):

Even when subsequent mechanical processing can be dispensed with by virtue of these measures, the method is technically exceptionally demanding since it is necessary to replace each individual rod in the aggressive bath in rotation. Furthermore, because of the rotation technically demanding solutions are required for transferring the generally very high electroplating current onto the rod, for example by means of brushes.

Brief Summary Text - BSTX (9):

Another solution to the sketched problem is described in the publication DE-AS 11 03 103. A device is presented there for partial electroplating of elongate cylindrical bodies (disc valve stems). These bodies are arranged concentrically in tube-shaped anodes and are secured at one end in a stepped metal core. The cathodic current is supplied via this metal core. The metal core is separated from the electrolytic cell by an insulating body. The metal core and the insulating body delimit the electroplating layer at the upper end of the item to be treated. The lower end is protected by a protective lacquer from unwanted electroplating.

Brief Summary Text - BSTX (10):

Since every single body to be electroplated must be individually secured in this embodiment and in addition since the protective lacquer for masking the

(12) **United States Patent**
Kauper et al.

(10) **Patent No.: US 6,168,691 B1**
(45) **Date of Patent: Jan. 2, 2001**

(54) **DEVICE FOR ELECTROCHEMICAL TREATMENT OF ELONGATE ARTICLES**

(75) Inventors: **Rudolf Kauper**, Schwanstetten; **Thomas Lummer**, Greding; **Wolfgang Richter**, Berlin; **Reinhard Silberhorn**, Burgthann; **Manfred Krepelka**, Berlin, all of (DE)

(73) Assignee: **Atotech Deutschland GmbH** (DE)

(*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

(21) Appl. No.: **09/170,356**

(22) Filed: **Oct. 13, 1998**

(30) **Foreign Application Priority Data**

Aug. 9, 1996 (DE) 196 32 132
Jan. 2, 1997 (DE) 197 22 983
Aug. 7, 1997 (WO) PCT/EP97/04341

(51) **Int. Cl.**[7] **C25D 17/00**
(52) **U.S. Cl.** **204/224 R**; 204/297.5; 204/272; 204/DIG. 7
(58) **Field of Search** 204/224 R, 297 W, 204/272, DIG. 7, 279, 278, 471, 297.05, 196.01

(56) **References Cited**

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0 196 251 10/1986 (EP) .
52-224700 10/1987 (JP) .

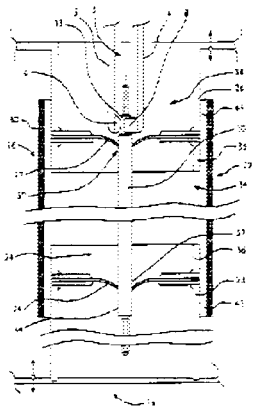
* cited by examiner

Primary Examiner—Kathryn Gorgos
Assistant Examiner—Wesley A. Nicolas
(74) *Attorney, Agent, or Firm*—Paul & Paul

(57) **ABSTRACT**

A method and a device are described for the electrochemical treatment of elongate articles, preferably bars. The article **10** is clamped at one end by means of a clamp **3** and is introduced into a hollow chamber that has a longitudinal axis, in an electrode **30**, arranged in a dip bath with a periphery parallel to the axis, in as concentrically axial a manner as possible and is thereby directed through at least one axially displaceable, perforated screening mask **23,26** so that part of the area not to be treated electrochemically is screened from the electrode. The article and electrode are connected to a current source. A container **14** for treatment liquid has at least one electrode **30** therein, the electrode having a hollow chamber with a longitudinal axis and a periphery parallel to the axis. The article is introduced into the hollow chamber. At lease one screening mask **23,26** is axially adjustable within the hollow chamber and has openings for introducing the article. The mask can prevent electrochemical treatment of the article in specific areas. A current source and electrical connections are provided to the electrode and to the article.

14 Claims, 6 Drawing Sheets



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222	US 0883756 A	5						☑				USOCR
	US 0881810 A	5						☑				USOCR
224	US 0875291 A	3						☑				USOCR
225	US 0861558 A	3						☑				USOCR
226	US 0836339 A	2						☑				USOCR
227	US 0827689 A	4						☑				USOCR
228	US 0817419 A	2						☑				USOCR

US-PAT-NO: 0881810

DOCUMENT-IDENTIFIER: US 0881810 A

TITLE: OCR SCANNED DOCUMENT

DATE-ISSUED: March 10, 1908

INVENTOR: Name not available

US-CL-CURRENT: 204/272, 205/151

NOOCRTEXT

No. 881,810. PATENTED MAR. 10, 1908.

G. A. LUTZ.

ELECTROPLATING APPARATUS.

APPLICATION FILED APR. 6, 1907.

2 SHEETS—SHEET 2.

Fig. 3

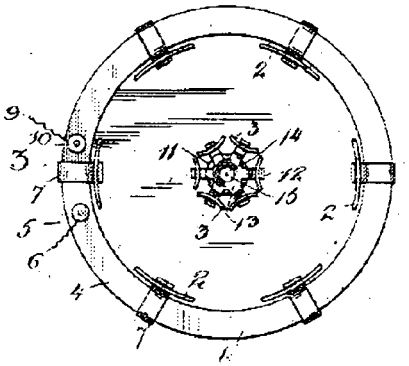
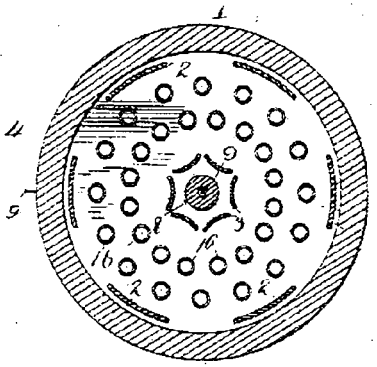


Fig. 4



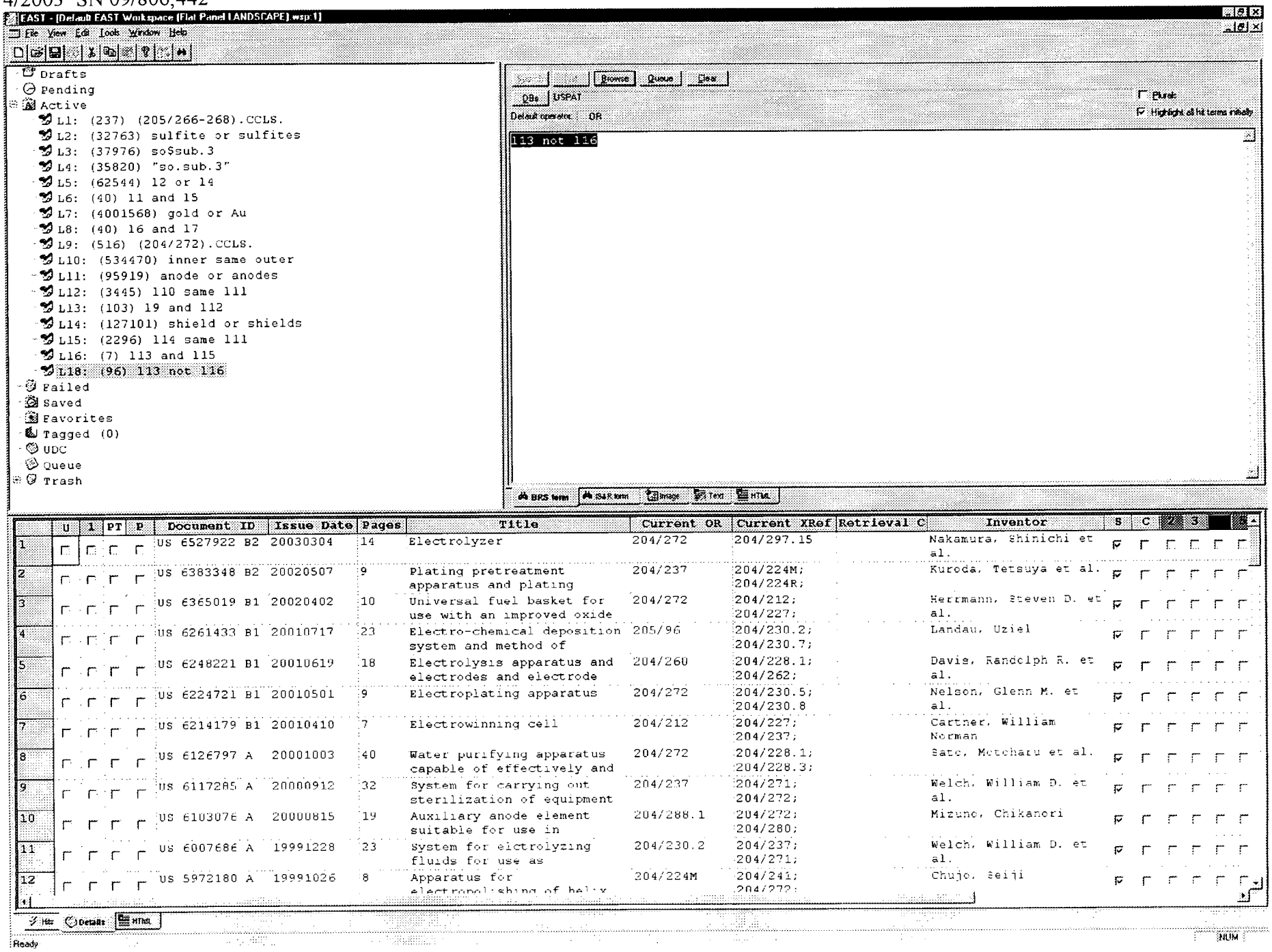
Witnesses.

Inventor

Geo. A. Lutz

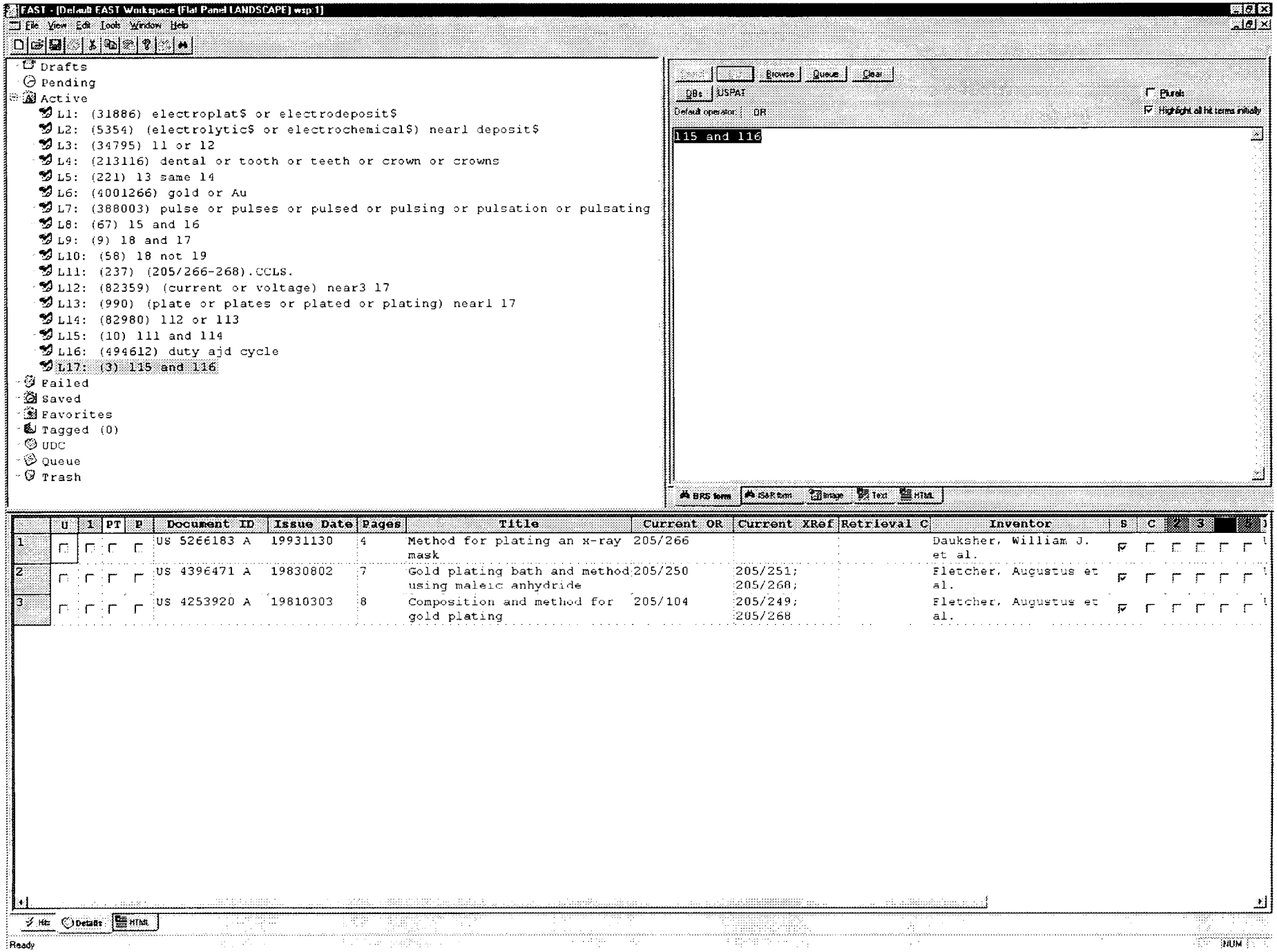
By his Attorneys

F. G. Bourne



	U	I	PT	P	Document ID	Issue Date	Pages	Title	Current OR	Current XRef	Retrieval C	Inventor	S	C	2	3
1	☐	☐	☐	☐	US 6527922 B2	20030304	14	Electrolyzer	204/272	204/297.15		Nakamura, Shinichi et al.	☑	☐	☐	☐
2	☐	☐	☐	☐	US 6383348 B2	20020507	9	Plating pretreatment apparatus and plating	204/237	204/224M; 204/224R;		Kuroda, Tetsuya et al.	☑	☐	☐	☐
3	☐	☐	☐	☐	US 6365019 B1	20020402	10	Universal fuel basket for use with an improved oxide	204/272	204/212; 204/227;		Herrmann, Steven D. et al.	☑	☐	☐	☐
4	☐	☐	☐	☐	US 6261433 B1	20010717	23	Electro-chemical deposition system and method of	205/96	204/230.2; 204/230.7;		Landau, Uziel	☑	☐	☐	☐
5	☐	☐	☐	☐	US 6248221 B1	20010619	18	Electrolysis apparatus and electrodes and electrode	204/260	204/228.1; 204/262;		Davis, Randolph R. et al.	☑	☐	☐	☐
6	☐	☐	☐	☐	US 6224721 B1	20010501	9	Electroplating apparatus	204/272	204/230.5; 204/230.8		Nelson, Glenn M. et al.	☑	☐	☐	☐
7	☐	☐	☐	☐	US 6214179 B1	20010410	7	Electrowinning cell	204/212	204/227; 204/237;		Cartner, William Norman	☑	☐	☐	☐
8	☐	☐	☐	☐	US 6126797 A	20001003	40	Water purifying apparatus capable of effectively and	204/272	204/228.1; 204/228.3;		Sato, Motoharu et al.	☑	☐	☐	☐
9	☐	☐	☐	☐	US 6117285 A	20000912	32	System for carrying out sterilization of equipment	204/237	204/271; 204/272;		Welch, William D. et al.	☑	☐	☐	☐
10	☐	☐	☐	☐	US 6103076 A	20000815	19	Auxiliary anode element suitable for use in	204/288.1	204/272; 204/280;		Mizuno, Chikanori	☑	☐	☐	☐
11	☐	☐	☐	☐	US 6007686 A	19991228	23	System for electrolyzing fluids for use as	204/230.2	204/237; 204/271;		Welch, William D. et al.	☑	☐	☐	☐
12	☐	☐	☐	☐	US 5972180 A	19991026	8	Apparatus for electropolishing of helix	204/224M	204/241; 204/272;		Chujo, Seiji	☑	☐	☐	☐

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L4: (213116) dental or tooth or teeth or crown or crowns
L5: (221) l3 same l4
L6: (4001266) gold or Au
L7: (388003) pulse or pulses or pulsed or pulsing or pulsation or pulsating
L8: (67) l5 and l6
L9: (9) l8 and l7
L10: (58) l8 not l9
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L12: (82359) (current or voltage) near3 l7
L13: (990) (plate or plates or plated or plating) near1 l7
L14: (82980) l12 or l13
L15: (10) l11 and l14
L16: (494612) duty adj cycle
L17: (3) l15 and l16
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Saved
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Tagged (0)
UDC
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Trash
Search
Clear
Browse
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1 US 5266183 A 19931130 4 Method for plating an x-ray mask 205/266 Dauksher, William J. et al.
2 US 4396471 A 19830802 7 Gold plating bath and method using maleic anhydride 205/250 205/251; 205/268; Fletcher, Augustus et al.
3 US 4253920 A 19810303 8 Composition and method for gold plating 205/104 205/249; 205/268 Fletcher, Augustus et al.
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1	US 6551485 B1	8										USPAT
2	US 6551483 B1	10										USPAT
3	US 6478943 B1	13										USPAT
4	US 6368482 B1	27										USPAT
5	US 6080504 A	10										USPAT
6	US 5972192 A	6										USPAT
7	US 5800930 A	6										USPAT

US-PAT-NO: 5972192

DOCUMENT-IDENTIFIER: US 5972192 A

TITLE: Pulse electroplating copper or copper alloys

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Detailed Description Text - DETX (4):

In pulse electroplating, the thickness of the diffusion layer formed at the solution-electrode interface during plating is reduced, since Cu ions diffuse to the cathode surface while the current pulse is off. Pulse electroplating is generally employed in metal finishing industries and comprises, in its simplest sense, metal deposition by pulse electrolysis, as by interrupted DC current, to electroplate parts. This is effected with a series of pulses of DC current of equal amplitude and duration in the same direction, separated by periods of zero current. The pulse rate (frequency) and ON and OFF interval x (duty cycle) are controllable to optimize electro-deposition in a particular situation. Pulse electroplating can be conducted by utilizing a constant current or with constant voltage pulses. In employing pulse electroplating in accordance with the present invention, one having ordinary skill in the art could easily optimize the relevant variables, such as the duty cycle, frequency and current density in a particular situation.

Detailed Description Text - DETX (17):

A pair of trenches were formed in a dielectric layer by a damascene technique. The trenches had a diameter of about 0.25 .mu.m and a diameter of about 0.4 .mu.m, each having an aspect ratio greater than 3:1. Cu was electroplated to fill both trenches by employing unipolar (i.e., forward) pulse plating with a duty cycle of about 10% to about 90%, frequency of about 1 to about 1000 Hz and a current density of about 5 to about 50 mA/cm.sup.2. The plating solution contained a brightener (MD.TM.) and leveling agent (MLO.TM.) at a concentration of 0.5 ml/l to 30 ml/l (MD) and 0.1 ml/l to 15 ml/l (MLO). The kinetics of the electroplating copper were observed after 20 seconds, 40 seconds and 80 seconds, confirming that electroplating occurred commencing at the bottom of each trench and progressed upwardly. Ion-beam imaging confirmed that both trenches were filled without defects and that a single Cu grain occupied the entirety of each trench.

Detailed Description Text - DETX (22):

cathodic duty cycle of about 10% to about 90%

Detailed Description Text - DETX (23):

anodic duty cycle of about 10% to about 90%

Claims Text - CLTX (10):

7. The method according to claim 1, wherein in at least one of the first,

United States Patent [19]

Dubin et al.

[11] **Patent Number: 5,972,192**

[45] **Date of Patent: Oct. 26, 1999**

[54] **PULSE ELECTROPLATING COPPER OR COPPER ALLOYS**

[75] Inventors: **Valery Dubin**, Cupertino; **Chiu Ting**, Saratoga; **Robin W. Cheung**, Cupertino, all of Calif.

[73] Assignee: **Advanced Micro Devices, Inc.**, Sunnyvale, Calif.

[21] Appl. No.: **08/898,089**

[22] Filed: **Jul. 23, 1997**

[51] **Int. Cl.**[6] **C25D 5/18**; H01L 21/445

[52] **U.S. Cl.** **205/101**; 205/103; 205/104; 205/123; 438/641

[58] **Field of Search** 205/101, 102, 205/103, 104, 75, 123; 438/641

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Primary Examiner—Donald R. Valentine

Assistant Examiner—William T. Leader

[57] **ABSTRACT**

High aspect ratio openings in excess of 3, such as trenches, via holes or contact holes, in a dielectric layer are voidlessly filled employing a pulse or forward-reverse pulse electroplating technique to deposit copper or a copper-base alloy. A leveling agent is incorporated in the electroplating composition to ensure that the opening is filled substantially sequentially from the bottom upwardly.

16 Claims, No Drawings

4/2003

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15	US 5141602 A	27							☑				USPAT

US-PAT-NO: 5203931

DOCUMENT-IDENTIFIER: US 5203931 A

TITLE: Electrodeposition of indium-thallium shape memory alloys

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Detailed Description Text - DETX (22):

The average current density is generally in the range of from about 2 mA/cm.sup.2 to about 35 mA/cm.sup.2. An increase in average current density has likewise been found to correspond to an increase in the deposition of indium relative to the deposition of thallium in this binary system. The average current is increased by increasing the peak current density or by increasing the duty cycle (duty cycle = [current on time]/[current on time plus current off time]). The composition of the deposited indium-thallium alloy can therefore be in part controlled by controlling the average current density. An increase in average current density, with other parameters held constant, results in an alloy of lower thallium content.

Detailed Description Text - DETX (23):

The alloy composition may also be in part controlled by variation of the pulse frequency of the pulsed current. An increase in off time has been found to correspond to a slight increase in thallium content. This effect is thought to be due in part to the fact that a longer off time provides a greater opportunity for migration of the more noble and generally more preferentially deposited thallium ions to the electrolyte-electrode interface. Additionally, a shorter off time corresponds to an overall increase in average current density which, as discussed above, results in an increase in relative indium deposition. Although on time and off time are not particularly critical parameters, it is preferred that both be maintained in the range of from about 10 msec to about 50 msec, with a duty cycle in the range of from about 30% to about 70%.

Detailed Description Text - DETX (27):

The quantity of alloy deposited is precisely controlled by controlling the total amount of current supplied, measured in ampere-hours. Ampere-hours are a function of deposition time, duty cycle, peak current density and average current density. An increase in total current supplied corresponds to an increase in deposit thickness.

Claims Text - CLTX (22):

13. A process as set forth in claim 11 wherein said pulsed current has a duty cycle of between about 30% and about 70%.

Current US Cross Reference Classification - CCXR (2):

205/104

US005203931A

United States Patent [19]

O'Keefe

[11] Patent Number: 5,203,931

[45] Date of Patent: Apr. 20, 1993

[54] ELECTRODEPOSITION OF INDIUM-THALLIUM SHAPE MEMORY ALLOYS

[75] Inventor: Thomas J. O'Keefe, Columbia, Mo.

[73] Assignee: University of Missouri, Columbia, Mo.

[21] Appl. No.: 763,343

[22] Filed: Sep. 20, 1991

[51] Int. Cl.[5] C25D 3/56; C25D 5/18

[52] U.S. Cl. 148/518; 148/563; 205/104; 205/238

[58] Field of Search 205/104, 238; 148/402, 148/563, 518

[56] References Cited

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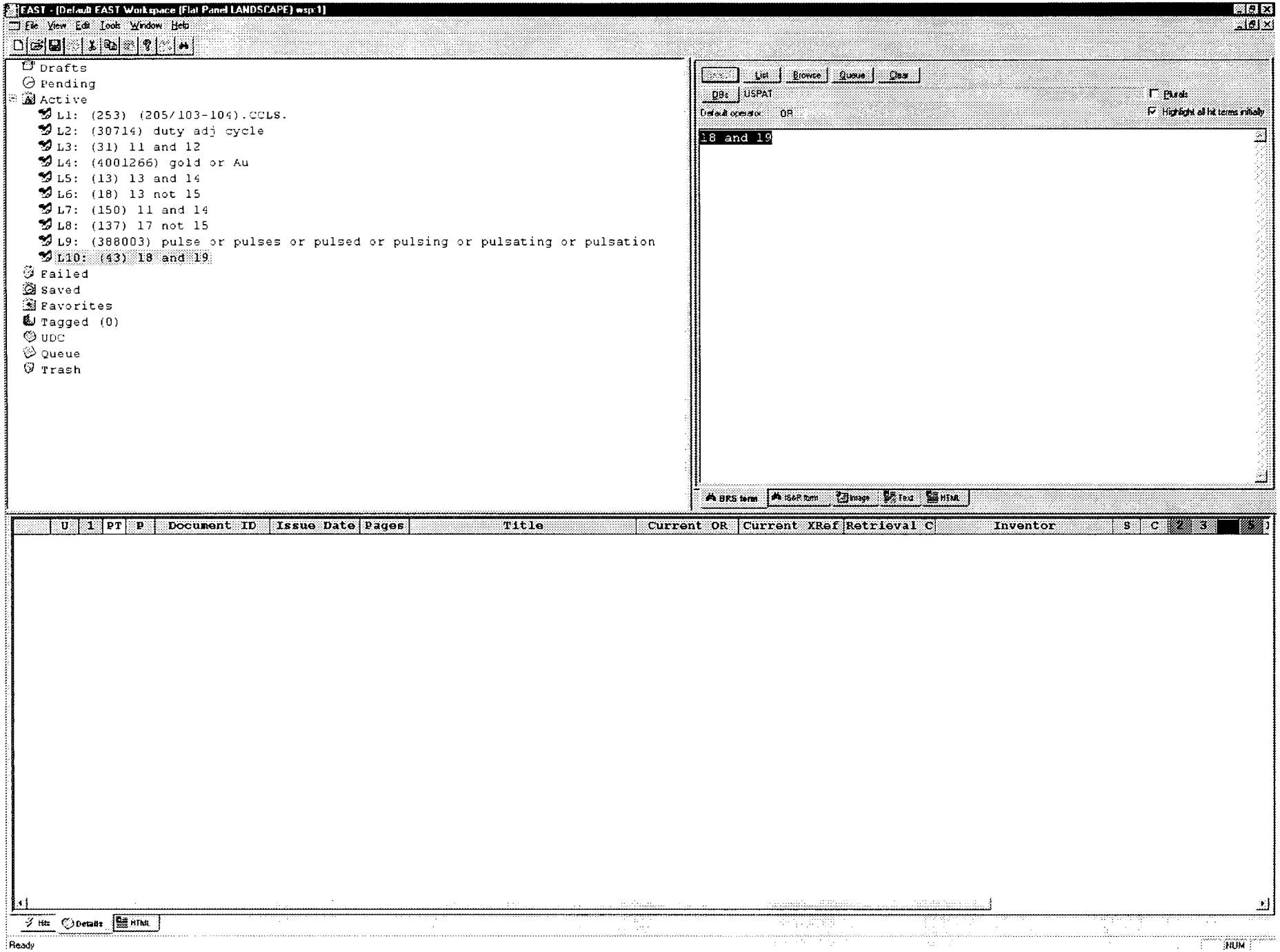
Primary Examiner—George Wyszomierski

Attorney, Agent, or Firm—Senninger, Powers, Leavitt & Roedel

[57] ABSTRACT

A process for preparing an indium-thallium alloy which exhibits shape memory transformation at a temperature greater than that temperature at which shape memory transformation would occur for a thermally prepared alloy of the same composition. The process includes providing an article for use as a cathode, providing an electrolyte which comprises indium and thallium ions, and electrodepositing an indium-thallium alloy having between about 21 and about 35 atomic percent thallium onto the article. A process for preparing an article constructed of an electrodeposited indium-thallium alloy which exhibits shape memory effect. An electrodeposited indium-based shape memory alloy.

14 Claims, 1 Drawing Sheet


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L1: (253) (205/103-104).CCLS.
L2: (30714) duty adj cycle
L3: (31) l1 and l2
L4: (4001266) gold or Au
L5: (13) l3 and l4
L6: (18) l3 not l5
L7: (150) l1 and l4
L8: (137) l7 not l5
L9: (388003) pulse or pulses or pulsed or pulsing or pulsating or pulsation
L10: (43) l8 and l9
Failed
Saved
Favorites
Tagged (0)
UDC
Queue
Trash
List
Browse
Queue
Clear
DBs
USPAT
Default operator:
OR
Plurals
Highlight all hit terms initially
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2	US 6482307 B2	16											USPAT
3	US 6478944 B1	13											USPAT
4	US 6447663 B1	10											USPAT
5	US 6440289 B1	9											USPAT
6	US 6402924 B1	7											USPAT
7	US 6387243 B1	12											USPAT

first time period, a second value for a second time period, and a third value for a third time period. These ratios may be also be varied in periodic cycles.

Detailed Description Text - DETX (5):

The choice of metal to be electrodeposited onto a substrate depends on the application. For example, copper is generally used as an undercoat for protection and/or conductivity, while gold is often used as a topcoat for decoration, protection and/or function, e.g., electrical contacts. Any one of a wide variety of metals can be used in the present invention, including tin, lead, palladium, gold, nickel, silver, zinc, copper, and alloys of two or more of these or other metals. The present invention is particularly useful for electrodepositing copper onto printed circuit boards with high aspect ratios, where aspect ratio is board thickness divided by hole diameter.

Detailed Description Text - DETX (7):

A pulse generating unit supplies a pulsed periodic reverse current which is applied across the electrodes of the plating cell. A typical pulse generating system generates a forward current of up to 800 amps and a reverse current of up to 2500 amps although other systems can be used. A switch mode rectifier which generates pulsed output with high energy reverse pulse is what is generally required for this invention.

Detailed Description Text - DETX (8):

Each system comprises a pulse engine and a separate control unit which sets and controls the pulse output in terms of a forward pulse time ranging from about 1 to 50 and preferably about 10 to 30 milliseconds; a reverse pulse time ranging from about 0.1 to 4 and preferably about 0.5 to 2 milliseconds; a forward peak current ranging from about 50 to 800 and preferably 100 to 300 amps; and a reverse peak current ranging from about 50 to 2500 and preferably about 400 to 1200 amps. A current density in the range of between 5 and 200 and preferably 20 to 100 ASF is typically used. Power is supplied for as long as is necessary to produce the desired deposits.

Detailed Description Text - DETX (10):

Pulse timing is then set and controlled from one controller which is configured as the master. Alternatively a personal or plant computer can be used to control all pulse units in the entire installation.

Detailed Description Text - DETX (11):

Pulse timing, average current density, and initial forward and reverse current densities may be either preset manually, or automatically set by the control unit. Average current density can be preset at a particular value, e.g, 33 amps per square feet, and power then supplied for the necessary time period, e.g., 45 minutes. A preferred pulse timing can be set, such as 20 milliseconds forward and 1 millisecond reverse.

Detailed Description Text - DETX (12):

(12) **United States Patent**
Martin et al.

(10) **Patent No.: US 6,402,924 B1**
(45) **Date of Patent: *Jun. 11, 2002**

(54) **PROGRAMMED PULSE ELECTROPLATING PROCESS**

(75) Inventors: **James L. Martin**, Merrick; **Stephane Menard**, Freeport; **David N. Michelen**, Brooklyn, all of NY (US)

(73) Assignee: **Shipley Company LLC**, Marlborough, MA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/561,883**

(22) Filed: **May 1, 2000**

Related U.S. Application Data

(63) Continuation of application No. 08/944,753, filed on Oct. 6, 1997, now Pat. No. 6,071,398.

(51) Int. Cl.[7] **C25D 5/18**

(52) U.S. Cl. **205/103**; 205/125; 205/296; 205/298; 205/920

(58) **Field of Search** 205/103, 125, 205/296, 297, 298, 920

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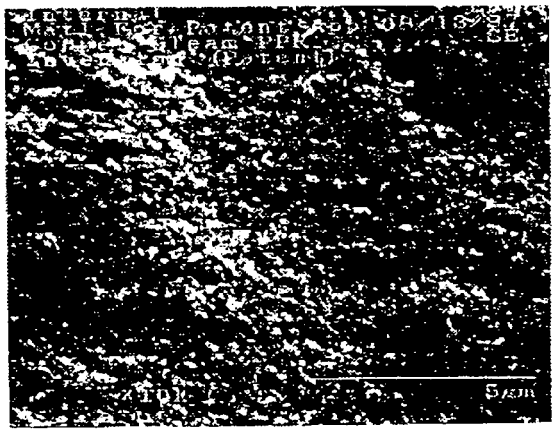
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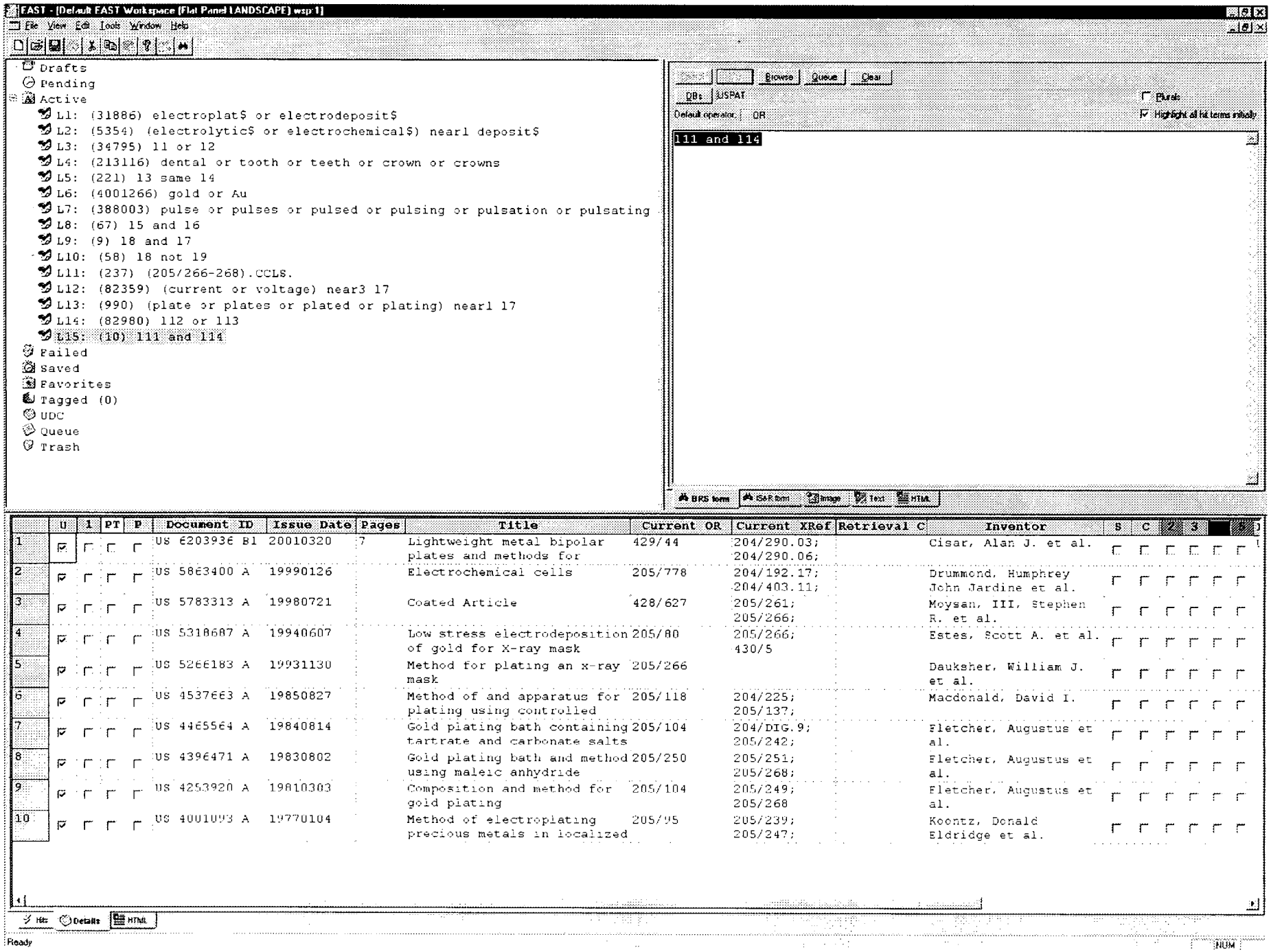
Primary Examiner—Donald R. Valentine
Assistant Examiner—William T. Leader
(74) *Attorney, Agent, or Firm*—Pennie & Edmonds LLP

(57) **ABSTRACT**

The present invention relates to a method of electrodepositing metal onto a substrate, which comprises applying a pulsed periodic reverse current across the electrodes of a plating cell utilizing a peak reverse current density and peak forward current density; and varying the ratio of peak reverse current density to peak forward current density in periodic cycles to provide metal deposits of uniform thickness and appearance upon the substrate. The invention also relates to a process for improving the properties of an electrodeposit, particularly on substrates having uneven surfaces or apertures, by using programmed pulse periodic reverse current modulation. More particularly, it involves varying the anodic to cathodic current density ratio, in order to improve the surface uniformity appearance, grain structure and levelling of the deposit while maintaining high current density throwing power.

10 Claims, 2 Drawing Sheets





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2	☑	☐	☐	☐	US 5863400 A	19990126		Electrochemical cells	205/778	204/192.17; 204/403.11;		Drummond, Humphrey John Jardine et al.	☐	☐	☐	☐
3	☑	☐	☐	☐	US 5783313 A	19980721		Coated Article	428/627	205/261; 205/266;		Moysan, III, Stephen R. et al.	☐	☐	☐	☐
4	☑	☐	☐	☐	US 5318687 A	19940607		Low stress electrodeposition of gold for X-ray mask	205/80	205/266; 430/5		Estes, Scott A. et al.	☐	☐	☐	☐
5	☑	☐	☐	☐	US 5266183 A	19931130		Method for plating an x-ray mask	205/266			Dauksher, William J. et al.	☐	☐	☐	☐
6	☑	☐	☐	☐	US 4537663 A	19850827		Method of and apparatus for plating using controlled	205/118	204/225; 205/137;		Macdonald, David I.	☐	☐	☐	☐
7	☑	☐	☐	☐	US 4465564 A	19840814		Gold plating bath containing tartrate and carbonate salts	205/104	204/DIG.9; 205/242;		Fletcher, Augustus et al.	☐	☐	☐	☐
8	☑	☐	☐	☐	US 4396471 A	19830802		Gold plating bath and method using maleic anhydride	205/250	205/251; 205/268;		Fletcher, Augustus et al.	☐	☐	☐	☐
9	☑	☐	☐	☐	US 4253920 A	19810303		Composition and method for gold plating	205/104	205/249; 205/268		Fletcher, Augustus et al.	☐	☐	☐	☐
10	☑	☐	☐	☐	US 4001093 A	19770104		Method of electroplating precious metals in localized	205/95	205/239; 205/247;		Koontz, Donald Eldridge et al.	☐	☐	☐	☐

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4	US 5318687 A	11						☑				USPAT
5	US 5266183 A	4						☑				USPAT
6	US 4537663 A	9					☑					USPAT
7	US 4465564 A	6					☑					USPAT

US-PAT-NO: 5266183

DOCUMENT-IDENTIFIER: US 5266183 A

TITLE: Method for plating an x-ray mask

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Detailed Description Text - DETX (6):

Typically, a substrate is placed in contact with the cathode of the electroplating system. A bias is applied between the anode and the cathode wherein the bias has a current density ranging between approximately 1 milliamp per square centimeter and 12 milliamps per square centimeter. Preferably, the bias is a pulsed current train having a frequency ranging between approximately 10 Hertz and 4,000 Hertz and having a duty cycle of at least 10%. Further, the pulsed current train may be modulated such that the pulsed current train is alternately on and off. For example, the pulsed current train may be on for a time ranging between approximately one and ten seconds, also referred to as an on-time, and off for a time ranging between approximately one millisecond and three seconds, also referred to as an off-time. It shall be understood that the type of bias is not a limitation of the present invention. In other words, the bias may be a DC bias. Application of the bias may form an electric double layer and a diffusion barrier between the anode and the cathode.

Detailed Description Text - DETX (9):

In a preferred embodiment, the electroplating solution has a pH of approximately 8.8, and a flow rate through the electroplating system of approximately 15 liters per minute. Further, in the preferred embodiment, a bias is provided as a current pulse train having a current density of approximately 3 milliamps per square centimeter, a frequency of approximately 700 Hertz and a duty cycle of approximately 25%. Further, the on-time of the pulsed current train is approximately ten seconds and the off-time of the pulsed current train is approximately one millisecond; wherein the duration of the bias, also referred to as an electrodeposition time, is approximately three minutes. It shall be understood that in the absence of the bias no appreciable plating occurs while the substrate is in the presence of the electroplating solution.

Claims Text - CLTX (7):

3. The method for plating an x-ray mask of claim 1 further including providing the bias as a pulsed current train having a frequency ranging between approximately 10 Hertz and 4,000 Hertz and duty cycle greater than approximately 10%.

Claims Text - CLTX (16):

applying a pulsed current train bias between an anode and a cathode wherein the pulsed current train bias has a current density ranging between approximately 1 milliamp per square centimeter and 12 milliamps per square centimeter, a frequency ranging between approximately 10 Hertz and 4,000 Hertz,

United States Patent [19]

Dauksher et al.

[11] **Patent Number: 5,266,183**

[45] **Date of Patent: Nov. 30, 1993**

[54] **METHOD FOR PLATING AN X-RAY MASK**

[75] Inventors: William J. Dauksher, Mesa; Douglas J. Resnick, Phoenix, both of Ariz.

[73] Assignee: Motorola, Inc., Schaumburg, Ill.

[21] Appl. No.: 881,111

[22] Filed: May 11, 1992

[51] Int. Cl.[5] C25D 3/48

[52] U.S. Cl. 205/266

[58] Field of Search 205/266

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Primary Examiner—T. M. Tufariello

Attorney, Agent, or Firm—Joe E. Barbee; Rennie William Dover

[57] **ABSTRACT**

A method for making an x-ray mask having a low-stress absorber layer. A substrate is placed in an electroplating system and an electroplating solution is provided to the electroplating system. The electroplating solution has a gold sulfite based component and a thallium based component. The thallium based component is at a concentration of at least 20 milligrams per liter of electroplating solution. A gold containing absorber layer is electrodeposited onto the substrate. A high concentration of thallium produces an absorber layer insensitive to the brightener concentration in the electroplating solution and having a stress less than approximately 1×10^8 dynes/cm^2. In addition, the absorber has a small grain size, a low surface roughness, and a low defect density. Thus, the absorber layer is easier to inspect and, if required, to repair.

13 Claims, No Drawings

4/2003

EAST Browser - L15: (10) 11 and 14 | US 4465564 | Tag: S | Doc: 7/10 (SORTED) | "Full" 1/6 (Total images 6)

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	Document ID	Pages	1	2	3		T	U	S	C	P	Kind Codes	Sou
5	US 5266183 A	4											USPAT
6	US 4537663 A	9											USPAT
7	US 4465564 A	6											USPAT
8	US 4396471 A	7											USPAT
9	US 4253920 A	8											USPAT
10	US 4001093 A	9											USPAT

US-PAT-NO: 4465564

DOCUMENT-IDENTIFIER: US 4465564 A

TITLE: Gold plating bath containing tartrate and carbonate salts

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Brief Summary Text - BSTX (7):

Despite the foregoing, a demand exists for a gold plating bath that is capable of producing electrodeposits of high purity, and particularly one that is capable of producing deposits of sufficient purity to meet the requirements of the semi-conductor industry, using either continuous or pulsed direct current. A need also exists for such a bath of relatively low specific gravity, which is capable of operating under high current density plating conditions at relatively low gold concentrations, and which has a high tolerance to contamination, such as from copper. Finally, there is a demand for a bath having the foregoing features and advantages, from which gold can be alloyed with various metals to produce a variety of characteristics in the deposit, and to extend the range of brightness exhibited thereby.

Brief Summary Text - BSTX (23):

Various types of plating apparatus may be employed in connection with the compositions and methods of the present invention, including equipment for barrel and rack plating, and for high speed continuous selective plating. In addition to steady direct current plating, pulse plating can be employed to produce good quality, non-porous deposits at relatively high speeds with the least amount of gold content.

Detailed Description Text - DETX (27):

The uncontaminated bath of Example Three above is tested for use in producing a semi-conductor package in which a silicon chip is bonded by heat and pressure to a gold electroplated surface, and the leads are electrically connected from the gold plated surface to the silicon chip by thermo-sonic or ultrasonic means. In the test, the surface for bonding is first plated with nickel from a sulfamate solution to a thickness of 1.25 micrometers, and is then plated in the gold bath to produce a 1.5 micrometer deposit, using either pulsed or nonpulsed DC current (average current density of 3 ASF). The resultant packages are subjected to standard wire bond test procedures used in the semi-conductor industry, involving evaluation of the assemblies in the "as plated" condition as well as after heat cycling at different temperatures and for varying periods, and satisfy all applicable criteria.

Claims Text - CLTX (11):

9. The method of claim 7 wherein said potential is applied by pulsed direct current.

United States Patent [19]

Fletcher et al.

[11] Patent Number: 4,465,564

[45] Date of Patent: Aug. 14, 1984

[54] GOLD PLATING BATH CONTAINING TARTRATE AND CARBONATE SALTS

[75] Inventors: Augustus Fletcher, Bristol, Conn.; David N. Cockayne, FanLing, Hong Kong; William L. Moriarty, South Meriden, Conn.

[73] Assignee: American Chemical & Refining Company, Inc., Waterbury, Conn.

[21] Appl. No.: 507,763

[22] Filed: Jun. 27, 1983

[51] Int. Cl.³ C25D 3/48; C25D 3/62

[52] U.S. Cl. 204/44; 204/43 G; 204/DIG. 9

[58] Field of Search 204/43 G, 46 G, 109, 204/123, 44, DIG. 9

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Primary Examiner—G. L. Kaplan

[57] ABSTRACT

A bath for electrodepositing gold utilizes, as the essential ingredients of its electrolyte, salts providing the tartrate radical and the carbonate radical. The bath will have a pH value ranging from approximately neutral to highly alkaline, and adjustments to lower the pH will most advantageously be made utilizing tartaric acid. The bath operates with relatively low gold concentrations, and is capable of producing highly pure deposits and highly desirable alloy deposits; it is especially well suited for semi-conductor industry applications.

15 Claims, No Drawings